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MICROELECTRODE GEOCHEMICAL OBSERVATORY FOR IN SITU MONITORING OF METALS CONCENTRATION AND MOBILITY IN CONTAMINATED SEDIMENTS

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14. ABSTRACT

The project objective was to demonstrate and validate the Analytical Instrument Systems, Inc. (AIS) microelectrode geochemical observatory (MGO) for the long-term monitoring of metals in contaminated sediments, including a laboratory phase and a pre-field deployment at Old Woman Creek (OWC) in Huron, OH. It became clear early on that adapting this open water technology for sediments application remains a challenge. Gold-mercury amalgam electrodes, built following a design from literature, were able to detect Fe, Mn, and reduced sulfur compounds, but not the Bremerton, WA site target metals: As, Cd, Cu, Pb, Hg, Zn. Five-mm gold electrodes fabricated following procedures from literature produced calibration curves for Cu, Pb, and Zn in standard solutions and for Pb and Zn in site porewater. Attempts to ruggedize the gold electrode proved futile as the gold wire was exceptionally fragile. Because OWC sediments contain mainly Mn and Fe, the MGO was deployed with the amalgam electrode. After a few days, the MGO began intermittently shutting down. The electrode fouled over a few weeks and produced incoherent, noisy scans. Further work is needed to design a rugged electrode with the required functionality across a broad range of metals that will support a field deployable probe. A refined field design will yield cost savings via alternative power sources, such as solar, and remote data collection capability.

15. SUBJECT TERMS

Sediments, metals, real-time monitoring, microelectrode geochemical observatory, MGO, gold, Au-Hg, amalgam, electrode

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FINAL REPORT

MICROELECTRODE GEOCHEMICAL OBSERVATORY FOR IN SITU MONITORING OF METALS CONCENTRATION AND MOBILITY IN CONTAMINATED SEDIMENTS

ESTCP Project Number: ER-201128

September 2013

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ABSTRACT

The Navy has identified over 150 contaminated sediment sites in its Installation Restoration (IR) and Base Realignment and Closure (BRAC) programs. Of these sites, approximately 25 to 30 percent have known or suspected metals contamination. Two common remediation strategies for metals contaminated sediments include capping and monitored natural remediation (MNR), which leave the contamination in place and therefore require long-term monitoring to evaluate remedy effectiveness. Given the extent of sediments contaminated by metals across the United States, and the costs associated with the sampling during long-term monitoring, there is a need for improved methods of in situ metals detection in sediments.

Electrochemical sensors have been tested in a wide range of aquatic settings, including marine sedimentary porewater; however, their use has been on time scales of hours to days. Long-term monitoring applications have not been evaluated (Luther et al., 1999). The objective of this study was to demonstrate and validate the Analytical Instrument Systems, Inc. (AIS) microelectrode geochemical observatory (MGO) for the long-term monitoring of metals in contaminated sediments.

The MGO was evaluated for performance criteria during a laboratory evaluation phase (8 months), and a pre-field deployment at Old Woman Creek (OWC), located in Huron, Ohio (1 month).

During the early stages of the laboratory testing, it became evident that the off-the-shelf SnapTrodes™ lacked both an accurate and precise response as well as the sensitivity to detect the selected target metals at their maximum contaminant level (MCL). After the SnapTrodes™ were found to be ineffective, gold-mercury amalgam electrodes were built following a design from literature. The electrode was able to detect iron, manganese, and reduced sulfur compounds but not the target metals. After testing the amalgam electrode, 5 mm gold electrodes were constructed following procedures from literature. The gold electrode was able to produce calibration curves for copper, lead, and zinc in standard solutions. The 5 mm gold electrodes were also able to produce calibration curves with lead and zinc in Bremerton porewater.

Attempts to ruggedize the gold electrode before field deployment proved futile as the gold wire was exceptionally fragile. The AIS system was deployed at OWC for 1 month. OWC is a relatively pristine wetland containing mainly manganese and iron in the sediment, as opposed to the target metals; therefore, the amalgam electrode was used at the site. The unit was able to detect manganese, iron, and reduced sulfur in the sediment for a few days before the system shut down. The system had to be restarted multiple times. In addition to hardware issues, the electrode became fouled over a relatively short period of time (weeks) and produced incoherent, noisy scans.

The proposed work was predicated on the off-the-shelf SnapTrode™ components functioning properly. While the team proposed using mature, commercially available components, it became clear during the initial phase of this project that adapting open water technology for sediments application remains a challenge. Although the team expanded on resident expertise by fabricating two different electrodes, further work is needed to design an electrode with the required functionality across a broad range of metals. Ruggedization of the electrode will support the design of a field deployable probe. Refinement of the field design will yield cost savings measures via alternative power sources, such as solar, and remote data collection capability. Each of these areas requires further, suitably-funded studies to advance this technology to a field-ready condition.

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LIST OF ACRONYMS AND ABBREVIATIONS

2-D	two-dimensional
AC	alternating current
AIS	Analytical Instrument Systems, Inc.
ASV	anodic stripping voltammetry
BNC	Bayonet Neill-Concelman
BRAC	Base Realignment and Closure
CLE-CSV	competitive ligand exchange-cathodic stripping voltammetry
CSV	cathodic stripping voltammetry
CV	coefficient of variation
DC	direct current
DPV	differential pulse voltammetry
DOC	dissolved organic carbon
DOM	dissolved organic material
ESTCP	Environmental Security Technology Certification Program
HMDE	hanging mercury drop electrode
ICP-MS	inductively coupled plasma mass spectrometry
IR	Installation Restoration
KCl	potassium chloride
MCB	Marine Corps Base
MCL	maximum concentration level
MGO	microelectrode geochemical observatory
MNR	monitored natural remediation
NOAA	National Oceanic and Atmospheric Administration
ORP	oxidation-reduction potential
OSU	Ohio State University
OU	operable unit
OWC	Old Woman Creek
PEEK	Polyether ether ketone
RSD	relative standard deviation
RV	research vessel
SD	standard deviation
SWV	square-wave voltammetry
U.S. EPA	U.S Environmental Protection Agency

1.0: INTRODUCTION

This report summarizes the project findings for ER-201128, Microelectrode Geochemical Observatory (MGO) for In-Situ Monitoring of Metals Concentration and Mobility in Contaminated Sediments. Project performance objectives, and specific tasks that address these objectives, including electrode testing, sediment characterization, and pre-field deployment activities are presented in this report and evaluated with respect to the stated success criteria and lessons learned.

1.1   Background

The Navy has identified over 150 contaminated sediment sites in its Installation Restoration (IR) and Base Realignment and Closure (BRAC) programs. Of these sites, approximately 25 to 30 percent have known or suspected metals contamination. Two common remediation strategies for metals contaminated sediments include capping and monitored natural remediation (MNR), which leave the contamination in place and therefore require long-term monitoring to evaluate remedy effectiveness. Given the extent of sediments contaminated by metals across the United States, and the costs associated with the sampling during long-term monitoring, there is a need for improved methods of in situ metals detection in sediments. Electrochemical sensors have been tested in a wide range of aquatic settings, including marine sedimentary porewater; however, their use has been on time scales of hours to days. Long-term monitoring applications have not been evaluated (Luther et al., 1999).

1.2   Project Objective

The objective of ER-201128 was to demonstrate and validate the Analytical Instrument Systems, Inc. (AIS) MGO to measure real-time in situ multiple metals species concentrations in synthetic and natural porewaters and sediments for use in long-term monitoring at sites with metals contamination. This project was envisaged with using commercially available components for a mature technology that has been successfully deployed on a regular basis in open water environments.

1.3   Brief Description of MGO

The MGO system was proposed to be comprised of up to eight individual, vertically spaced ports of solid-state electrochemical sensors that are able to be programmed to detect those metals of interest at a particular site. The MGO was proposed to be tailored to site-specific depth intervals, with several microelectrodes spaced according to the sampling requirements; capturing porewater concentrations in the native sediments, cap layer, and the overlying water. Each probe would be engineered within a cylindrical housing structure, approximately 4-in diameter, with the length determined by the site-specific requirements (Figure 1-1). Theoretically, this system could be capable of nearly continuous monitoring of dissolved metals, including selectivity for speciation of metals with different oxidation states (e.g., As(III) and As(V)) and promised to provide monitoring data to site managers to capture long-term trends.

This project's MGO design is based on the AIS DLK system. The AIS microelectrodes have only been deployed in marine environments. The AIS design is based upon the work of Luther et al. (2008) as a guide. Of those electrochemical sensors commonly deployed in the field, gold-mercury amalgam electrodes are sensitive to the widest range of metal species, and are the standard working electrode for the MGO. Glassy carbon electrodes are sensitive to mercury, and could be used in situations where mercury is a metal of concern. AIS deployed gold-mercury amalgam microelectrodes (in seawater for a period of 55 [in the lab] to 120 days deployed in a coastal environment). Stable readings were reported over this time period for both events (Luther et al., 2008). These electrodes are designed to evaluate

multiple metal species in one electrochemical scan assuming that the redox couples of the analytes are sufficiently different. Ultimately, each target metal has a different electrochemical response, dependent largely on the surface properties of the working electrode.

Each MGO, inclusive of the pH/temp/oxidation-reduction potential (ORP) probes and microelectrodes, could be networked to a single surface unit with waterproof cable. Operational control could be conducted wirelessly via a main surface unit, which could be mounted within a buoy overlying the in-place sediment micro-observatory. The unit power source could also be housed within the main surface unit, and could consist of a 12-V battery interfaced with a small solar panel to charge the battery. The surface unit could be capable of data logging and wireless transmission of data, as well as real-time controls of the submerged system, such that diagnostics and troubleshooting can be conducted remotely.
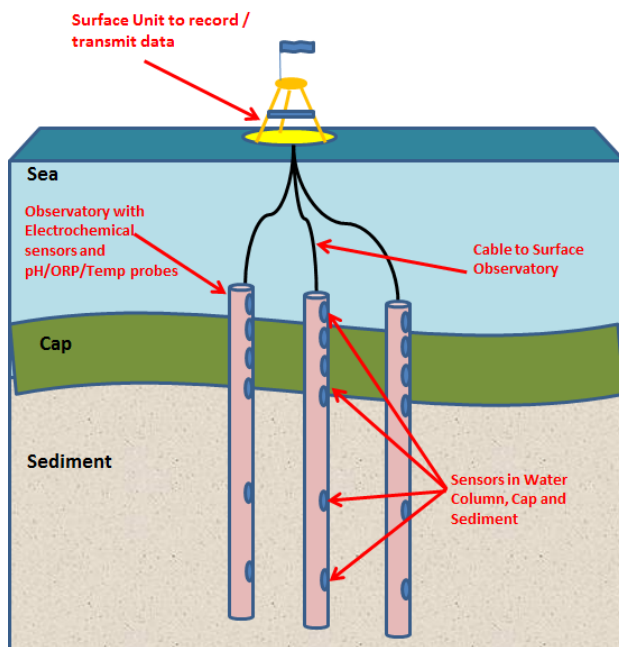
Figure 1-1. Schematic of MGO Deployed in the Field

2.0: PERFORMANCE OBJECTIVES

Performance criteria for the MGO electrode with respect to accuracy, precision, linearity, stability, and longevity under laboratory conditions in a variety of media, including standard solutions, site porewaters and site sediments, and under field conditions are detailed in Table 2-1.

The AIS electrode was tested in the laboratory with metals spiked synthetic marine porewater, and with marine porewater and sediment that was collected by extruding core samples. Electrode testing was done in triplicate with standards solutions and porewater that were spiked with metals. The electrode was evaluated in solutions spiked with metals at a minimum of four concentrations per metal. The electrode was tested in sediment to measure background levels of metals and also with sediment spiked at 10-times background levels. The success criteria for the standard solution and porewater tests were to achieve a recovery between 90 and 110 percent, a coefficient of variation of less than 10 percent, and an R^2 value of greater than 0.9. The electrode was also deployed in the field for a period of one month to determine ease of use, maintenance issues, and the impact of fouling on the electrode longevity.

Table 2-1. Performance Objectives

Performance Objective	Matrix	Methods	Data Requirements	Success Criteria
Accuracy: Recovery (R) = Measurement /Reference x 100% Precision: Relative Standard Deviation (RSD) = Standard Deviation (SD)/Average Measurement Linearity: plot of measurements vs concentrations	Standard solutions	Preparation of solutions for copper, zinc, mercury, cadmium, and lead at 0.01X, 0.10X, 1X, and 10X the metals Maximum Contaminant Level (MCL). Preparation of solutions with iron, reduced sulfur compounds, and manganese. Spike concentrations confirmed by ICP-MS.	7 metals and reduced sulfur compounds At least 4 concentrations 3 replicates	Average R: 90-110% Average RSD: < 10% $R^2 > 0.90$
Accuracy: Recovery (R) = Measurement/Reference x 100% (No Spike) Recovery (R) = (Measurement with Spike–Background)/ Spike (With Spike) Precision: RSD = SD/Average Measurement	Porewater - Bremerton	Porewater matrices centrifuged from Bremerton sediments; measured background levels of Cd, Hg, Pb, Fe, Mn, and Zn in porewater collected from at least 4 depths in the core samples. Spiked at 10X the background level if no contamination was present.	8 cores, extruded cores and collected the porewater for electrode testing. 3 metals (Zn, Cu, and Pb) At least 4 concentrations 3 replicates	Average R: 90-110% Average RSD: < 10% $R^2 > 0.90$
Accuracy: Recovery (R) = Measurement /Reference x 100% (No Spike) Recovery (R) = (Measurement with Spike–Background)/ Spike (With Spike) Precision: RSD = SD/Average Measurement	Sediment - Bremerton	Calibration of electrodes using *ex situ* standards. Sediments analyzed for target metals by *in situ* voltammetry and compared to ICP-MS of spikes.	3 metals evaluated (Cu, Pb, and Zn). Background plus 10X spike 3 replicates	Average R: 70-130% Average RSD: < 30%

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Table 2-1. Performance Objectives (Continued)

Performance Objective	Matrix	Methods	Data Requirements	Success Criteria
Control charting (average +/- 2 SD warning limit; +/- 3 SD action limit based on above data) Electrode longevity	Solutions and sediments	Measure the stability and robustness of microelectrodes as a function of time.	Measure background levels of metals for a period of one month in solutions and sediments. Spike sediment at 10X the background levels if metals are not detected.	Stop measurements and perform corrective action if measurements fall above/below a 2 SD warning limit
Qualitative Performance Objectives				
Ease of deployment and autonomous performance	Field deployment at Old Woman Creek	Feedback from graduate student conducting the research as well as the designer of the MGO (AIS); MGO able to function over prescribed time autonomously with minimal intervention by the graduate student, AIS, or P.I.s.	Continuous monitoring at field sites for one month.	Ease of use Calibration, maintenance, downtime Electrode longevity Impact of fouling

3.0: TASK RELATED ACTIVITIES

This section presents various task activities:

- Electrode testing, including evaluation of the commercial SnapTrode™ and subsequent fabrication of gold and gold-mercury amalgam polyether ether ketone (PEEK) electrodes,

- Sediment collection and characterization at Bremerton Naval Complex, Bremerton, WA,

- Voltammeter evaluation for use in the field, and

- Field unit construction and deployment at Old Woman Creek (OWC) National Estuarine Research Reserve (a part of the National Oceanic and Atmospheric Administration [NOAA]), located in Huron, OH.

A Gantt chart showing the dates of the project's major activities is presented in Figure 3-1.

Activities	10/11-12/11	1/12-2/12	3/12-4/12	5/12-6/12	7/12-8/12	9/12-10/12	11/12-12/12	1/13-2/13	3/13-4/13	5/13-6/13
Testing SnapTrode™	────	────	───►							
Comparison to hanging mercury drop electrode (HMDE)	────	────	────	────	───►					
Building and testing Hg-amalgam electrode			────	────	────	────	────	────	────	───►
Bremerton sampling			───►							
Bremerton porewater analysis				────	───►					
Design, construction, and testing of gold wire electrode							────	────	───►	
Deployment of partially ruggedized voltammeter to Old Woman Creek									───►	
Sediment porewater study								────	───►	
Assessment of deployed data									──►	
Writing of the Interim Report								────	────	───►

Figure 3-1. Gantt Chart of Project Activities

3.1 Electrode Testing

The laboratory evaluation phase involved testing the off-the-shelf SnapTrode™, constructing gold and gold-mercury amalgam electrodes, calibrating the microelectrodes with a characterization of metals distribution in synthetic (0.54 molar [M] potassium chloride [KCl]) and natural porewaters collected from Bremerton Naval Complex, and investigating electrode longevity and potential fouling issues. Electrodes were calibrated in both metal spiked standard solutions and Bremerton porewater at five concentrations in triplicate analysis. Calibration of metals sensors was conducted through direct comparison of metals data obtained by the electrochemical sensors with the reference HMDE and conventional ICP-MS analysis. The success criteria for the calibration tests were to achieve a recovery between 90 and 110 percent, a coefficient of variation of less than 10 percent, and an R^2 value of greater than 0.9. Electrodes were also tested in Bremerton sediment to determine a recovery between 90 and 110 percent, and a coefficient of variation of less than 30 percent for metals spiked in sediment at 10-times the background levels.

To facilitate understanding of the challenges involved in electrode testing, Subsections 3.1.1 through 3.1.3 focus on commercial electrode performance, fabrication of electrodes in the laboratory and ruggedization efforts for the fabricated electrode. Subsections 3.1.4 through 3.1.6 focus on electrode performance in standard solutions, porewaters, and intact sediment cores.

3.1.1   SnapTrode™ Testing. SnapTrodes™ were tested in the laboratory to assess precision, accuracy and linearity with metals spiked into synthetic marine porewater. The SnapTrodes™ were tested in lead, copper, and zinc spiked synthetic porewater (0.54 M KCl). The off-the-shelf electrodes were also tested with iron and manganese; however, after months of evaluation, the electrochemical scans showed very poor correlation with the reference HMDE scans.

Hundreds of thousands of scans were conducted during the evaluation of the off-the shelf electrode. The electrode could not detect the most easily analyzed target metals (lead, copper, and zinc), so it was determined that it was beyond the electrode's capabilities to measure the other target metals (mercury, cadmium, nickel, chromium, and silver). Furthermore, it was determined that the electrodes would not be able to detect oxyanions (e.g., arsenate, arsenite, chromate, bichromate, and selenate). A representative poor scan with a SnapTrode™ in a lead spiked standard solution is shown in Appendix A.

3.1.2   PEEK Electrode Fabrication and Testing. In June 2012, a staff member from OSU accompanied Don Nuzzio (AIS Inc.) on a research trip aboard the Research Vessel (RV) Savannah to learn about PEEK electrode fabrication and polishing techniques. During the trip, the OSU staff member was trained on the polishing, plating, and testing techniques for the gold-mercury amalgam electrodes. Electrodes were fabricated from PEEK tubing, gold wire, and epoxy resin. Electrode tips were polished with a series of diamond polishing pastes and then amalgamated with mercury.

All of the data collected were benchmarked to established electrochemical scans using a HMDE. After getting poor results with the SnapTrodes™, two styles of electrodes were fabricated based upon the work of Brendel and Luther (1995):

- A 100 µm diameter and 0 mm protrusion gold with mercury amalgam PEEK electrode, and
- A second electrode, a 100 µm diameter and 5 mm protrusion, gold PEEK electrode.

The gold-mercury amalgam electrode was evaluated first. The electrode had poor reproducibility and stability of square-wave voltammetry (SWV) scans, and poor linearity in both low (0 to 195 nanomolar [nM]) and high (195 to 3,900 nM) metal concentration ranges; however, it was able to detect manganese, iron, and reduced sulfur compounds in solutions with concentrations ranging from 10 to 100s micromolar (µM). If the electrode failed, new electrodes were fabricated and tested using the techniques learned on

the research trip; however, fabricating new electrodes still resulted in poor electrochemical scans. There were also significant maintenance and preparation requirements for the gold-mercury amalgam PEEK electrode. A representative poor scan using a gold-mercury amalgam electrode in a lead spiked standard solution is shown in Appendix A.

The gold electrode was able to produce data with good accuracy, precision and linearity for some metals. The constructed gold probe had significantly reduced preparation and maintenance requirements in comparison with the gold-mercury amalgam electrode, and was ruggedized with a plastic frit. Figure 3-2 shows the comparison of the SnapTrodes™ and PEEK electrodes.
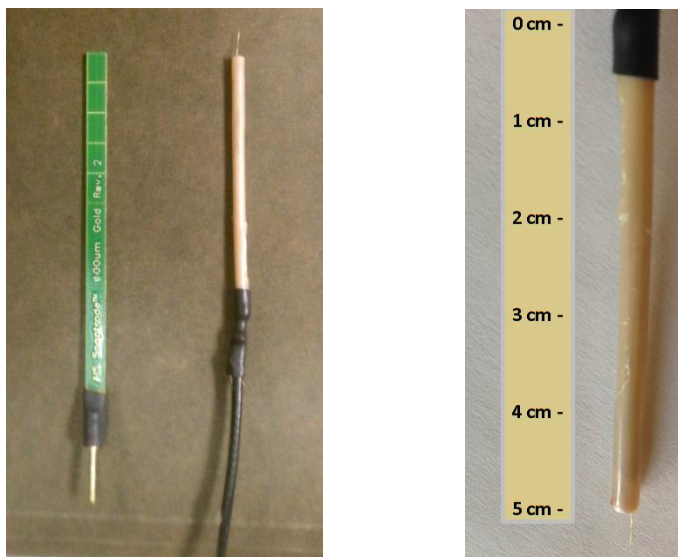
Courtesy Ohio State University

Figure 3-2. SnapTrodes™ and PEEK Electrode (left); PEEK Electrode with Scale (right)

3.1.3   Electrode Longevity and Ruggedization. The electrode tips had to be ruggedized before conducting sediment tests and the pre-field deployment. The electrode tips were ruggedized by testing a porous tube with approximately a 60 to 70 micron pore size which was large enough to allow water to flow freely through it (Figure 3-3). The bottom of the tube was sealed and the tube was attached to the PEEK electrode using epoxy. Multiple scans showed either no signal for the target metals or poor reproducibility.
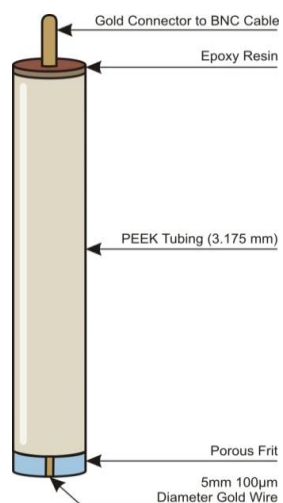
Courtesy Ohio State University

**Figure 3-3. Schematic of the 5-mm Gold Electrode Ruggedized with a Porous Frit (left);
Gold Electrode with Frit (right)**

In an early test of field-readiness of the electrodes, a 1.5 meter stainless steel spear was fabricated with a solid aluminum cone attached on one end. The electrode was affixed to the shaft using a tie-strip, and the cone acted to shelter the electrode as the spear was driven into the sediment at OWC (Figure 3-4). Further attempts to ruggedize the electrodes included fitting a porous tube over the 5 mm gold electrode; however, this tubing interfered with the electrochemical scans and was not used in the field.

Figure 3-4. A Steel Rod with an Aluminum Tip was Fabricated to Shelter the Electrode Tip

Courtesy Ohio State University

3.1.4   Standard Solution Test. After assessing the performance of the electrodes, and determining that the modified gold PEEK electrode produced the most accurate and precise electrochemical scans for the target list of metals, standard solutions were prepared with the metals listed in Table 3-1 (U.S. Environmental Protection Agency [U.S. EPA] National Recommend Water Quality Criteria List). The test solutions were spiked at different multiples of the metal's acute marine MCL. The Demonstration Plan stated the amount spiked for each metal would be 0.01, 0.1, 1, and 10 times the acute marine U.S. EPA criteria level; however, some metals were spiked at different amounts to produce a broader range of

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the concentrations for preparing the calibration curves. For example, lead was spiked at 2, 5, 10, 50, and 100 times the acute marine U.S. EPA MCL.

Table 3-1. U.S. EPA National Recommended Water Quality Criteria for Selected Metals

| Metals | U.S. EPA Criteria (µg/L)[a] | | | |
| | Freshwater | | Marine | |
	Chronic	Acute	Chronic	Acute
Arsenic	340	150	69	36
Cadmium	2.0	0.25	40	8.8
Chromium (hexavalent)	16	11	1,100	50
Chromium (trivalent)	570	74	ND[b]	ND
Copper	ND	ND	4.8	3.1
Lead	65	2.5	210	8.1
Mercury	1.4	0.77	1.8	0.94
Nickel	470	52	74	8.2
Selenium	ND	5	290	71
Silver	3.2	ND	1.9	ND
Zinc	120	120	90	81

(a) Standards are from U.S. EPA (except where noted). U.S. EPA criteria available from: http://www.epa.gov/waterscience/criteria/wqctable/.
(b) ND indicates that criteria are not defined.

Solutions were prepared in synthetic marine porewater at a concentration of 0.54 M KCl. The solutions were spiked with metals at five concentrations and in triplicate. Before calibration, the electrodes were initially screened for overall scan quality, and signal position and strength using standard metal solutions with known potentials. The data requirements were modified to test six metals. The metals tested were:

- copper,
- lead,
- zinc,
- mercury,
- cadmium, and
- manganese.

Manganese was tested as historical data showed that the porewater at OWC had high concentrations of manganese and did not contain any of the target metals. Further, the gold-mercury amalgam PEEK electrode was used for the manganese testing because it was able to detect manganese better than the gold electrode. Manganese was tested in a 0.02 M NaCl solution.

The standard solutions were scanned using the AIS Model DLK-70 Electrochemical Analyzer. The system used SWV (100 millivolts [mV]/s) for the analysis. The potential range scanned varied for each analyte. Zinc scanned from -1.8 to 2.0 volts (V) with a sample time of 38,750 microseconds. Copper and lead scanned from -0.4 to 0.6 V in 10,000 microseconds. Manganese scanned from -0.1 to -1.8 V in 8,750 microseconds. The metal solutions were also preserved in nitric acid and sent for ICP-MS analysis to OSU's Trace Element Research Laboratory.

The percent recovery was determined by comparing the tested target metal concentrations to the ICP-MS data. Calibration curves were developed by graphing the average peak height in amperes to the metal concentration. A trendline with the R^2 values were added to the curves. The data were compiled and

compared to the success criteria for the tests. The success criteria for the tests consisted of achieving a percent recovery of between 90 and 110 percent, a coefficient of variation (CV) of less than 10 percent, and an R^2 greater than 0.9. The calibration data, calibration curves, and electrochemical scans are presented in Appendix B for the standard solution tests. Furthermore, a poor representative scan for cadmium using the gold electrode is shown in Appendix A.

3.1.5   Porewater Tests. The 5 mm gold electrodes were calibrated in Bremerton porewater with lead, copper, and zinc at five concentrations and in triplicate. As with the standard solution tests, the data requirements for the porewater tests were modified from testing seven metals to three metals. The lead and zinc concentrations ranged from 8.0 to 81.0 and 81.0 to 811 µg/L, respectively. The porewater was spiked with 5.0 µM of copper (the highest concentration calibrated in standard solutions) and was not detected by the 5 mm gold electrode. The porewater was tested using the same procedures and equipment as the standard solutions tests. Lead and zinc were scanned from -1.8 to 1.2 and -1.8 to 2.0 V, respectively. Furthermore, the porewater tests had the same success criteria as the standard solution tests. Porewater from OWC was not tested.   The calibration data, calibration curves, and electrochemical scans are presented in Appendix C for the porewater tests.

3.1.6   Intact Sediment Core Tests. A portion of the Bremerton sediment was hydraulically extruded into a 250 mL Nalgene bottle. A 5 mm gold electrode was inserted 1 cm deep along with the counter and reference electrodes. No metals were detected, as no contaminant metals were present in the sediment. The sediment was then spiked using 1.2 mL of 10.4 mg/L (30.0 µM) lead nitrate stock solution. After spiking the sediment, the electrode did not detect the presence of any metals. The sediment was spiked 10 more times. No metals were detected by the 5 mm gold electrode in the sediment. The success criteria for the test were to achieve a percent recovery of between 90 and 110 percent and a CV of less than 30 percent. Spiked sediment samples were not analyzed for metals by ICP-MS since no metals were detected by the electrode. A representative poor scan using a 5 mm gold electrode in Bremerton sediment is shown in Appendix A.

3.2   Bremerton Sediment Collection and Characterization

Bremerton Naval Complex is a near shore marine embayment. The site had a previously characterized vertical distribution of metals contamination in the sediment (arsenic, cadmium, copper, lead, mercury, and zinc), easy access to sediments, and well defined sediment-cap layers.

In April 2012, eight cores were collected from Bremerton Naval Complex at OU 2B using a vibracore (Figure 3-5). Sediments were collected from a stable surface sampling platform on a subcontracted vessel. The corers were fitted with 8 feet of polycarbonate core liner. Once the cores were collected, they were cut at a point approximately 10 cm above the cap-sediment interface. The cores were capped, sealed and sent back via overnight express to OSU under ice and stored at 4°C.

The cores were extruded at OSU using hydraulic pressure and the sediment divided into 5 cm sections (Figure 3-6). The core collected from Station 3 was unable to be extruded due to the presence of coarse sand. The sediment sections were centrifuged and the porewater supernatant was decanted. Decanted porewater samples were filtered with 0.45 µm nylon filters. The filtered porewaters were analyzed using ICP-MS for cadmium, mercury, lead, iron, manganese, and zinc. Manganese, iron and zinc were detected above the detection limit. Conductivity was measured in five porewater samples. The pH, ORP, and DOC were not measured. pH and ORP electrodes were not available to take the measurements *in situ*. Once the porewaters were separated, equilibration with carbon dioxide in air rendered such measurements meaningless. The measurement of DOC was not necessary for the success of this project. The metals concentrations in the porewater at various depths were plotted and are presented in Appendix D.
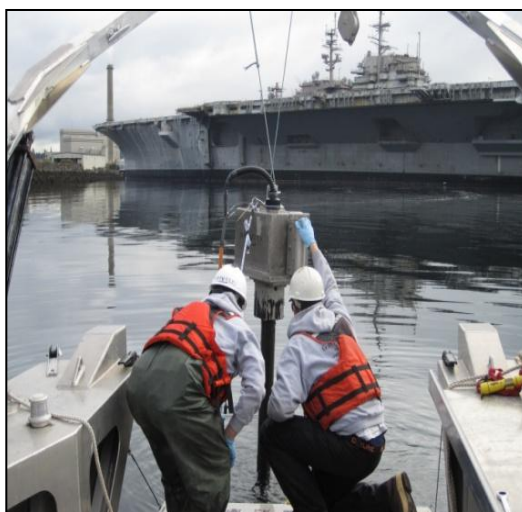
Courtesy Ohio State University

Figure 3-5. Core Sample Locations at Bremerton Naval Complex (top); Core Collection Using a Vibracore Mounted on a Vessel (bottom)

Courtesy Ohio State University

**Figure 3-6. Core Sample in Polycarbonate Liners (left);
Cores Sectioned into 5 cm Segments (right)**

## 3.3   Voltammetry Evaluation for Use in the Field

Voltammetry is an electro-analytical method that detects metals through changes in their oxidation state as a function of applied potential. As analytes are reduced or oxidized at a specific potential (measured in volts) the resultant current (i) is measured in amperes. The amount of current generated is proportional to the analyte concentration. Unlike potentiometry, which measures changes in the potential of a solution in response to the presence of an analyte, voltammetry is much more sensitive (pico to nanomolar vs. micro to millimolar) and can analyze multiple analytes using one electrode (an "ion-selective" electrode is needed in potentiometry and can only be used for that specific substance). The best example of a potentiometry application is the measurement of pH.

The type of voltammetry employed by this project is known as "polarography", which utilizes a mercury or mercury-amalgam "working" electrode coupled with a reference and counter electrode. The working electrode is where the potential is applied and where the redox chemistry of the analytes takes place. The reference electrode is basically a "half cell" (the other being the working electrode) with a known potential and no current goes through this electrode. The counter electrode balances (or "counters") the current generated at the working electrode.

There are many types of voltammetry/polarography in use today including linear sweep, SWV, cyclic, anodic stripping voltammetry (ASV), and cathodic stripping voltammetry (CSV) modes. ASV and CSV follow two main steps: a pre-concentration of the analyte onto the electrode surface after reduction followed by a stripping (oxidation) of the accumulated metal back into the solution phase. Using these methods detection limits below µg/L can be achieved. In order to increase speed and sensitivity, differential pulse voltammetry (DPV) and SWV can be applied to both ASV and CSV. DPV measures current at two points for each pulse of applied voltage, the first point just before the pulse and the second point at the end of the pulse. The differential reading of the current generates a peak-shaped voltammogram. SWV uses a symmetrical square wave pulse in which current is sampled two times at the end of the two half-waves. The generated peak height on the voltammogram is directly proportional to the concentration of the electroactive specie. Using voltammetric method SWV in conjunction with ASV and CSV (called square wave stripping voltammetry or SWSV), the limits of detection for the target metals could be found to be well below federal water quality standards. The team had to adapt to a combination of these methods to optimize electrode sensitivity and precision.

3.4 Field Unit Construction and Deployment at OWC

The laboratory testing and pre-field deployment utilized the AIS Model DLK-70 potentiostat. The system consists of a voltammeter with Bayonet Neill–Concelman (BNC) cable connections, SnapTrodes™ (a 100 µm gold electrode plated with elemental mercury), a reference (Ag/AgCl) electrode, and a counter (Pt) electrode (Figure 3-7). The system operated on the DLK-70 Web-PStat™ software. Before pre-field deployment, the unit was partially ruggedized at OSU using a Pelican case.
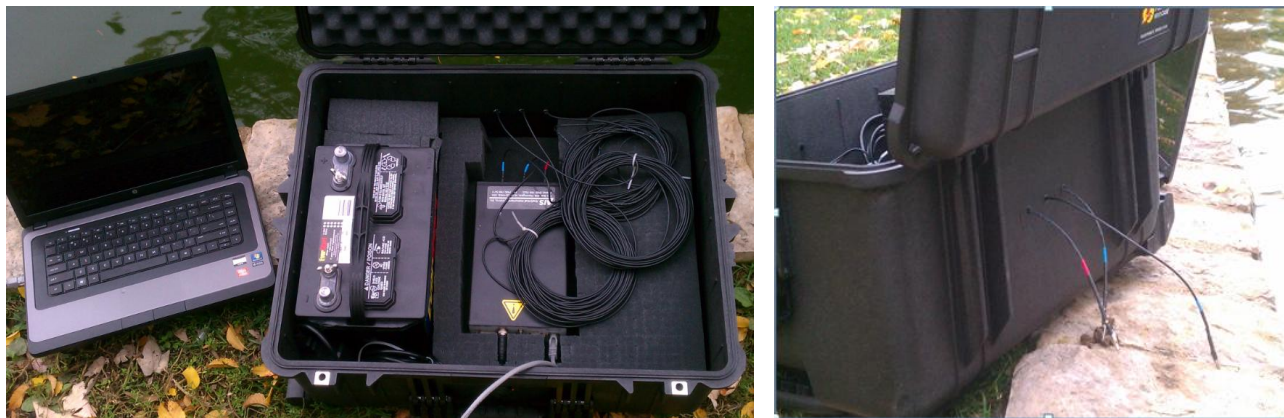
Courtesy Ohio State University

Figure 3-7. AIS Model DLK-70 with DC Source (left); Microelectrode; Counter, and Reference Electrode are Connected to the DLK-70 (right)

3.4.1 Lab Testing of DLK70. Pre-field deployment activities involved ruggedizing the instrument (hardware, electrodes, and cables), constructing the steel rod to drive the electrode into the sediment, and testing the DLK-70 in auto-scan mode for extended periods of time (approximately a week). Issues regarding the potentiostat itself included the instrument freezing unexpectedly while in auto-scan mode. During extended tests in auto-scan mode, the system would freeze approximately 10 percent of the time due to unknown software problems. The entire system had to be restarted to reinitiate the scans. The reasons for the software malfunction were never resolved and were ultimately detrimental to success of the pre-field deployment. Lab use determined that the DLK system had to be frequently reset such that remote monitoring for periods of time exceeding 1 week was untenable. Furthermore, excessive instrument noise was observed originating from the power source (see the section below). It was discovered that these problems were exacerbated by using alternating current (AC) and not having cables that were properly shielded.

3.4.2 Deployment at OWC. Severe winter weather, issues getting the probe to work in the lab, and delays in renting another DLK-70 resulted in several months of delay. On March 4, 2013, the DLK-70E was deployed at the OWC field site in Huron, OH. The DLK-70E was equipped with three gold-mercury amalgam electrodes (working, reference, and counter). The amalgam electrode was deployed as opposed to the gold wire electrode because the porewater at OWC contained manganese and iron, and no target metals.

The laptop driving the DLK-70 E was housed in a toolshed on site and powered by an outlet (Figure 3-8). The instrument was powered by two car batteries. The car batteries worked well in the field as a direct current (DC) source. DC power had to be used to power the system as AC resulted in noisy signals. The batteries were replaced as one became exhausted. The proposal originally stated using a 12-V battery

interfaced with a small solar panel to charge the battery. The solar panel was not tested. The DLK-70E was placed in a waterproof case and stored in the toolshed.

The field unit was deployed at a predetermined location at OWC away from pedestrian traffic. The electrodes were deployed in the sediment by using a machined steel rod with an aluminum cone at the end. The electrode was affixed to the rod using tie-strips. The rod was manually driven into the sediment to a depth of approximately 1 foot. The cone served to shelter the electrode tip as the rod was driven into the sediment. Cables were ruggedized and made waterproof by wrapping the connections between the BNC cable and the electrodes with 3M™ electrical tape and further coating the connections with liquid electrical tape. The electrode tip was not fitted with a porous tube, as the tube was found to be detrimental to electrode performance in lab tests.

Weekly inspections were performed on the instrument. The inspections included checking the cables for environmental damages and cycling the power to the DLK-70. During this time, the deep cycle marine battery was switched to a fully charged battery.   Electrochemical scans from OWC are shown in Appendix E.

The zip file accompanying this report contains the raw electrochemical data (current versus voltage) for the standard solution tests, porewater tests, representative poor scans, and the OWC field deployment.

Courtesy Ohio State University

Figure 3-8. The Gold-Mercury Amalgam Electrode was Affixed to Steel Rod with an Aluminum Point (top); A Toolshed with Laptop and DLK-70E at OWC (left); The Rod with Electrode was Driven into the Sediment at OWC (right)

4.0: RESULTS AND DISCUSSION

This section contains the major results from the laboratory testing and pre-field deployment. Issues with the performance of the technology, and recommendations and lessons learned will also be discussed.

4.1 Results

This section provides details on evaluating the performance objectives, testing the PEEK electrodes in standard solutions and Bremerton porewater for target metals, and electrode component cost information.

4.1.1 Evaluation of Performance Objectives. The planned performance objectives stated in the Demonstration Plan and the actual tests are presented in Table 4-1. The table also contains the findings associated with each performance objective. More specific discussions of findings for electrode evaluation in standard solutions and porewater are presented in the following subsections.

Table 4-1. Tests and Findings of the Performance Objectives

Performance Objective	Success Criteria	Tests	Findings
Quantitative Performance Objectives – Synthetic and Natural Porewaters (Lab Tests)			
Recovery, Accuracy, Calibration of metals-spiked standard solutions and porewater	Recovery = 90-110% CV < 10% $R^2 > 0.9$	**0.54 M KCl Standard Solution**: The SnapTrode™ was tested with iron, manganese, lead, copper and zinc. Copper, zinc, lead, mercury, and cadmium were tested with the 5 mm gold electrode. Lead, copper, zinc, manganese, iron, and reduced sulfur compounds were tested with the gold-mercury amalgam electrode. **Bremerton Porewater:** Measurements for zinc, copper, and lead were made with the 5 mm gold electrode and all the target metals were measured by ICP-MS. In addition, the HMDE was used to measure zinc, lead, and copper. **OWC Porewater:** NA	**0.54 M KCl Standard Solution**: The SnapTrode™ was not able to detect any of the tested metals. It was determined that it would also not work for oxyanions (e.g., arsenate, arsenite, chromate, bichromate, and selenate). The electrodes were not sensitive to mercury, cadmium, nickel, chromium, and silver. Gold-mercury amalgam electrodes detected manganese, iron, and sulfur compounds. Lead, zinc, and copper were detected by the gold wire electrode. **Bremerton Porewater**: Lead and zinc were detected by the 5 mm gold electrode at the MCL. Copper was not detected. **OWC Porewater:** NA
Quantitative Performance Objectives – Intact Sediment Cores (Lab Tests)			
Recovery, Accuracy, Calibration of metals-spiked sediments	Recovery = 90-110% CV < 30%	**Bremerton Sediment**: Copper, zinc, and lead were measured by gold electrode. **OWC Sediment**: NA	**Bremerton Sediment**: No target metals were detected by gold electrodes. Sediment samples were not analyzed for metals by ICP-MS as no metals were detected. **OWC Sediment**: NA

Table 4-1. Tests and Findings of the Performance Objectives (Continued)

Performance Objective	Success Criteria	Tests	Findings
Quantitative Performance Objectives – Control Charting (Lab Tests)			
Control charting electrode longevity	± 2 SD	Due to technical issues there was insufficient time to thoroughly test the micro-electrodes using solutions. Sediments were done concurrent to the criteria in the preceding row.	No target metals were detected in the sediments.
Quantitative Performance Objectives – Pre-Field Deployment at Old Woman Creek, Huron, Ohio			
Ease of deployment and autonomous performance	Ease of use Calibration, maintenance, downtime Electrode longevity Impact of fouling	Gold-mercury amalgam electrodes were deployed in sediments at OWC for 1 month starting from March 4, 2013.	Microelectrodes collected data twice an hour for two days before shutting down. After restart, it continued to collect data, albeit much noisier and less reliable than before.

4.1.2   Calibration of Standard Solutions. The metals tested in standard solutions were copper, lead, zinc, mercury, cadmium, and manganese. The commercial SnapTrode™ was unable to detect any of the tested metals and it did not work for oxyanions (e.g., arsenate, arsenite, chromate, bichromate, and selenate). The 5 mm gold electrodes were able to detect the following metals in 0.54 M KCl: copper, lead, and zinc. Gold-mercury amalgam electrodes were used for manganese calibration in a 0.02 M NaCl solution.

The calibrations met the success criteria of an R^2 value greater than 0.9 for all manganese, copper, lead, and zinc. In addition, all metals except zinc had an average coefficient of variation of less than 10 percent. ICP-MS data determined that all the tested concentrations for manganese met the success criteria by having a recovery between 90 and 110 percent. The recovery for copper, lead, and zinc ranged from 82.7 to 85.9%, 87.3 to 158.9%, and 92.1 to 129%, respectively. The success criteria are tabulated for each metal in Table 4-2. Green highlighted data indicate success criteria were met. Red highlighted data indicate success criteria were not met.

Table 4-2. Success Criteria for Standard Solutions

Metal Calibrated	Standard Solution	Electrode Type	Concentration Range (µg/L)	Success Criteria R² > 0.9	Success Criteria Coefficient of Variation < 10%	Success Criteria Recovery 90-110%
Mn	0.02 M NaCl	Gold-mercury amalgam	5,490	0.98	9.1%	97.8%
			10,980		4.1%	97.4%
			16,470		2.0%	98.5%
			21,960		1.3% / Average CV: 4.1%	101%
Cu	0.54 M KCl	5mm gold	64	0.99	13.3%	82.8%
			127		8.1%	85.9%
			191		7.9%	83.1%
			254		5.3%	85.0%
			318		3.1% / Average CV: 7.5%	82.7%
Pb	0.54 M KCl	5mm gold	8	0.95	9.8%	159%
			16		9.4%	121%
			40		3.4%	93.9%
			81		0.7%	87.3%
			404		3.2%	NA
			808		1.1% / Average CV: 4.6%	NA
Zn	0.54 M KCl	5mm gold	81	0.98	23.5%	98.0%
			162		16.0%	92.1%
			405		9.3%	116%
			811		1.6% / Average CV: 12.6%	129%
Cd	0.54 M KCl	5mm gold	4.4	0.21	30.0%	NA
			8.8		27.0%	NA
			18		44.0%	NA
			44		52.0%	NA
			88		21.0% / Average CV: 34.8%	NA
Hg	0.54 M KCl	5mm gold	0.5	0.08	44.0%	NA
			1.0		30.0%	NA
			2.0		93.0%	NA
			5.0		1,627% / Average CV: 449%	NA

Green: Met Criteria; Red: Did not Meet Criteria

4.1.3   Calibration and Characterization of Bremerton Porewater. Eight cores were collected from Bremerton Naval Complex. Filtered porewater was analyzed for cadmium, mercury, lead, iron, manganese, and zinc by ICP-MS (plots of the metals concentrations versus depth are presented in Appendix D, the porewater data is tabulated in Appendix F). Porewater could not be extracted from Core Station 3 due to the presence of coarse sand. The depth intervals for the porewater samples are presented in Table 4-3. Iron, manganese, and zinc were detected in all porewater samples. Metal concentrations across the seven cores had significant variability, but tended to decrease with depth with the exception of zinc. Zinc concentrations were uniform across all cores, generally between 100 and 600 µg/L. In general, zinc concentrations were the highest in the vertical extent from 5 to 10 cm with a maximum zinc concentration of 594 µg/L occurring at Core Station 1. Iron (8,290 µg/L) and manganese (1,092 µg/L)

were detected at their highest concentrations at the sediment surface (1-5 cm) at Core Stations 2 and 8, respectively.

The conductivity was measured in five Bremerton porewater samples before conducting voltammetry testing. The porewater was filtered with 0.45 μm nylon filters before ICP-MS analysis and the conductivity measurements. The conductivity measurements are shown in Table 4-4.

Table 4-3. Depth Intervals of Porewater Samples

Core Station	Depth Intervals of Samples
Core H- Station 1	1-5 cm, 6-10 cm, 11-15 cm, 16-20 cm
Core G- Station 2	1-5 cm, 6-10 cm, 11-15 cm, 16-20 cm, 21-25 cm, 26-30 cm
Core A- Station 3	Samples could not be extruded due to the presence of coarse sand.
Core B- Station 4	1-5 cm, 6-10 cm, 11-15 cm, 16-20 cm, 21-25 cm
Core C- Station 5	1-5 cm, 6-10 cm, 11-15 cm, 16-20 cm, 21-25 cm, 26-30 cm
Core D- Station 6	1-5 cm, 6-10 cm, 11-15 cm, 16-20 cm, 21-25 cm, 26-30 cm, 31-35 cm
Core E- Station 7	1-5 cm, 6-10 cm, 11-15 cm, 16-20 cm, 21-25 cm
Core F- Station 8	1-5 cm, 6-10 cm, 11-15 cm, 16-20 cm, 21-25 cm, 26-30 cm, 31-35 cm

Table 4-4. Conductivity Measurements in Bremerton Porewater

Core Station	Core Section Depth (cm)	Conductivity (mS/cm)
Core Station 2	6-10	37.7
Core Station 4	6-10	35.9
Core Station 5	6-10	37.5
Core Station 6	21-25	35.6
Core Station 8	6-10	37.0

The metals tested in Bremerton porewater were copper, lead, and zinc. The 5 mm gold electrodes were able to detect lead and zinc but not copper. Lead and zinc achieved R^2 values greater than 0.9; however, the average CV was greater than 10 percent for both metals. The recovery for lead and zinc ranged from 96.0 to 122% and 112 to 370 %, respectively, for the tested concentrations. The recovery for zinc was high due to the blank porewater containing 324 μg/L of zinc. The success criteria for the porewater tests are presented in Table 4-5. Green highlighted data indicate success criteria were met. Red highlighted data indicate success criteria were not met.

Table 4-5. Success Criteria for Bremerton Porewater

Metal Calibrated	Electrode Type	Concentration Range (µg/L)	Success Criteria		
			$R^2 > 0.9$	Coefficient of Variation < 10%	Recovery 90-110%[a]
Pb	5mm gold	8.0	0.98	61.9%	96.0%
		16.0		19.6%	103%
		40.0		8.8%	14.9%
		81.0		25.4%	122%
				Average CV: 28.9%	
Zn	5mm gold	81.0	0.93	31.2%	370%
		162.0		45.6%	219%
		405.0		3.8%	138%
		811.0		21.6%	112%
				Average CV: 25.6%	

(a) The blank Bremerton porewater had 324 µg/L of zinc.
Green: Met Criteria; Red: Did not Meet Criteria

4.1.4 **Cost Associated with Electrode Fabrication.** The material costs and labor associated with constructing the SnapTrode™ and gold electrode are presented in Table 4-6. The gold electrode had significantly reduced preparation requirements and material costs associated with its construction in comparison to the SnapTrode™.

Table 4-6. Costs Associated with the AIS SnapTrode™ and 5 mm Gold PEEK Electrode

Item	Price
Material Costs	
AIS SnapTrode™	
AIS SnapTrode™	$125.00
2-foot BNC Cable	$10.00
Polishing Materials	$3.00
Mercuric Nitrate	$0.50
Total SnapTrode™ Material Cost	**$138.50**
5 mm Gold PEEK Electrode	
2-foot BNC Cable	$10.00
West Systems Epoxy Resin/Hardener	$0.26
0.1 mm Gold Wire	$1.23
PEEK Tubing	$1.17
Gold Pins	$2.00
60/40 Resin-Core Solder	$0.10
Total PEEK Electrode Material Cost	**$14.76**
Labor	
AIS SnapTrode™	
Test SnapTrodes™; Polish; Amalgamate, and polarize	60-90 minutes per electrode
5 mm Gold PEEK Electrode	
Fabricate and Test Electrode	20-30 minutes per electrode

5.0: DISCUSSION OF TECHNOLOGY PERFORMANCE AND SUMMARY OF LESSONS LEARNED

The original proposal for the ESTCP project was predicated on the target metals being able to be assayed by voltammetry using off-the-shelf components that could be assembled into the MGO. Through the course of the project it became apparent that the off-the-shelf SnapTrode™ was ineffective as it lacked both an accurate and precise response as well as the sensitivity to detect the target metals at the stated MCL. The research team determined that since the MCL could not be achieved for the most easily analyzed target metals (e.g., lead, copper, and zinc) that the remaining, more difficult to measure, metals, especially the oxyanions were beyond the capabilities of the off-the-shelf components.

In light of this, the team opted to build its own mercury amalgam electrodes using the design published by Brendel and Luther (1995). After real hands-on experience on an oceanographic research cruise, the team became exceptionally proficient at the building and testing of these electrodes. The team found that they easily detected iron and manganese ranging from 10 to 100 µM, but detection of the other metals proved elusive. For example, lead was detectable, but not reproducible with respect to current response and potential position. Thus, the team opted to not pursue this approach for the target analytes identified in the ESTCP proposal.

After extensive mining of the literature search, the team opted on an exposed gold wire design first proposed in the 1980s. The gold wire approach worked in that reproducible standard curves were available for three target metals (zinc, copper, and lead), but could only achieve MCL for zinc and lead. Multiple attempts at ruggedizing the electrode proved futile as the gold wire was exceptionally fragile.

The last stage of the project involved assessment of the deployed system at OWC. A nearby relatively pristine wetland, with copious levels of iron and manganese, was chosen for deployment. Mercury amalgam electrodes were used as they worked well for these two metals. The unit initially worked for a few days before shutting down. The system shut down multiple times over a relatively short time span (weeks). The electrodes also became fouled or poisoned and simply stopped working. At present, no explanation is available for this occurrence.

In conclusion, the proposed work as originally written was dependent on the off-the-shelf components working. When this was found to not be the case, it forced the team to redesign the entire system. At this point, the remotely deployed electrodes cannot work to detect deleterious metals in a reliable fashion and the electrode itself needs to be redesigned.

5.1   DLK-70E Potentiostat

This project was envisaged with using commercially available components for a mature technology that has been successfully deployed on a regular basis in open water environments. The team did not anticipate the failure of the commercial electrode to perform satisfactorily and the need to design and fabricate new electrodes. This unforeseen obstacle, along with the challenges of ruggedizing the electrode, significantly reduced the resources available for the design of the field unit and comprised the viability of the field deployment at OWC.

A fully deployable potentiostat was not ordered as proposed in the proposal. A Pelican case was used to partially ruggedize the laboratory grade DLK-70E potentiostat. However, it was deployed exposed to the full force of the elements due to the inability to ruggedize the laptop computer needed to drive the instrument. Thus, the system could only be run in a sheltered tool shed at the field deployment site where power was available to drive the laptop computer. Further, it was determined that a marine grade battery was needed to power the DLK-70E. While the power draw on the battery was low, it nonetheless needed

to be monitored every few days and a new battery had to be swapped out on the time scale of days to up to a week.

The DLK-70E operated in automated scan mode, but periodically "froze" for no apparent reason. The "freezing" episodes were able to be decreased by cutting down on the number of scans performed to one or two per hour. On a practical scale, this was more than a sufficient number of scans. Nonetheless, after roughly 24 hours of deployment, the instrument froze up and required manual reboots. Thus, it is believed that the instrument in its current form would be unreliable for long-term deployment.

5.2   Electrode Performance

The team had to manufacture several electrodes before producing one that would operate satisfactorily in the field. Each electrode was tested prior to insertion into the sediment by scans in the overlying water column to detect for both oxygen and hydrogen peroxide. Once in the sediment, the electrodes worked well and were able to detect redox active species; however, after the first and subsequent "freezing" events, the electrode performance degraded. Over the time interval of the deployment, the electrodes continued to degrade and there were episodes where they recorded only noise. Thus, the mercury amalgam electrode, as built, was able to detect redox active species in the field for which it was designed (iron, manganese, and sulfur), but its performance deteriorated over time. The gold wire electrode was not deployed as the ruggedized housing designed to protect the delicate electrode surface failed in lab bench tests. A summary of the electrode testing is presented in Table 5-1.

Table 5-1. Summary of Electrode Testing

Electrode Type	Metals Tested	Laboratory Tests			Field Deployment
		Standard Solution (0.54 M KCl)	Bremerton Porewater	Bremerton Sediment	Old Woman Creek[a]
SnapTrode™	Lead	↓	NA	NA	NA
	Zinc	↓	NA	NA	NA
	Copper	↓	NA	NA	NA
	Iron	↓	NA	NA	NA
	Manganese	↓	NA	NA	NA
Gold-Mercury Amalgam	Lead	↓	NA	NA	NA
	Zinc	↓	NA	NA	NA
	Copper	↓	NA	NA	NA
	Iron	↑	NA	NA	↓
	Manganese	↑	NA	NA	↓
	Reduced Sulfur Compounds	↑	NA	NA	↓
5 mm Gold	Lead	↑	↑	↓	NA
	Zinc	↑	↑	↓	NA
	Copper	↑	↓	↓	NA
	Mercury	↓	NA	NA	NA
	Cadmium	↓	NA	NA	NA

(a) The amalgam electrode worked at OWC for the first couple of days but stopped working as the electrode tip became fouled.

NA: Not Applicable

5.3   Recommendations and Lessons Learned

The MGO as originally proposed by the manufacturer, AIS, was not able to deliver on expectations based upon the team's experiences during the testing. This project was based on the use of "off-the-shelf" components, but the SnapTrode™ did not detect any of the target metals, requiring the project to expend resources to design and fabricate electrodes.

Polarography using the gold-mercury amalgam electrode was unable to adequately detect the analytes of interest with any type of sensitivity or precision, while the non-deployable hanging mercury drop electrode was highly successful for detecting many (but not all) of the target species. In the proposal, the team believed that the gold-mercury amalgam electrode tip was capable of acting in a manner similar to a hanging mercury drop electrode, whereby both ASV and CSV could be used to analyze the respective cation and oxyanion analytes. As demonstrated in this report, the gold-mercury amalgam electrode tip failed to measure any of the target analytes with any degree of reliability with the exception of manganese, sulfur, and iron species. Finally, the presence of naturally occurring ligands would shift the potential at which the target analytes were detected (because the complexes have different half-cell potentials relative to the uncomplexed metal). The degree to which this occurred was dependent upon the

nature of the ligands present, which is unknown given that these ligands were part of the dissolved organic matter (DOM) pool and little to nothing is known about their composition. The entire system would need to be redesigned from the bottom up if such a technology can be deployed in the future.

In an effort to test other electrodes, it was found that the gold wire electrode in voltammetric mode was able to detect some of the analytes, but sensitivity, precision, and reliability varied from metal to metal. Further, the inability to design a proper ruggedized housing hampered efforts to deploy the electrode. Finally, lab testing of the electrode in actual porewaters was influenced by the presence of natural ligands that affected the potential at which current was measured. This made it difficult to pinpoint the exact nature of the analyte.

At present, long-term monitoring of sediments involves intrusive sediment coring that can disrupt the structural integrity of caps. Coring-based monitoring approaches are labor intensive and require careful handling of the cores to avoid compromising the sediments. Such approaches tend to be expensive and are designed to provide data on an annual or semi-annual basis. Less disruptive and more cost-effective technologies need to be developed and evaluated, as sediment sites are generally in long-term monitoring programs.

While the team proposed using mature, commercially available components, it became clear during the initial phase of this project that adapting open water technology for sediments application remains a challenge. Although the team expanded on resident expertise by fabricating two different electrodes, further work is needed to design an electrode with the required functionality across a broad range of metals. Ruggedization of the electrode will support the design of a field deployable probe. Refinement of the field design will yield cost savings measures via alternative power sources, such as solar, and remote data collection capability. Each of these areas requires further, suitably-funded studies to advance this technology to a field-ready condition.

5.3.1   Conclusions

- This project was envisaged with using commercially available components for a mature technology that has been successfully deployed on a regular basis in open water environments. The team did not anticipate the failure of the commercial electrode to perform satisfactorily and the need to design and fabricate new electrodes. This unforeseen obstacle, along with the challenges of ruggedizing the electrode, significantly reduced the resources available for the design of the field unit and comprised the viability of the field deployment at OWC.

- The commercial SnapTrode™ did not function as anticipated for detecting the target metals.

- The fabricated gold-mercury amalgam electrode was able to detect iron, manganese, and reduced sulfur compounds but not the target metals.

- The fabricated gold electrode was not able to produce accurate and reproducible scans for mercury and cadmium, but did produce calibration curves for copper, lead, zinc, and manganese.

- The fabricated gold electrode was calibrated with lead, copper, and zinc in Bremerton porewater and was able to detect lead and zinc in the porewater.

- The fabricated gold electrode was unable to detect zinc, copper, and lead in Bremerton sediment. The DLK-70 was not effective in long-term measurement of analytes at OWC.

- Further work is needed to design a sensitive, reliable, rugged electrode for application in a field deployable probe for sediments metals monitoring. At present, gold electrodes hold the most promise.

6.0: LITERATURE CITED

Brendel, P.J. and G.W. Luther, III. 1995. "Development of a Gold Amalgam Voltammetric Microelectrode for Determination of Dissolved Fe, Mn, O^2, and S (-II) in Porewaters of Marine and Freshwater Sediments," *Environ. Sci. Technol.* 29: 751-761.

Luther, G.W. III, C.E. Reimers, D.B. Nuzzio, and D. Lovalvo. 1999. "In Situ Deployment of Voltammetric, Potentiometric, and Amperometric Microelectrodes from a ROV to Determine Dissolved O^2, Mn, Fe S (-II), and pH in Porewaters," *Environmental Science and Technology,* 33:4352-4356.

Luther, G.W. III, B.T. Glazer, S. Ma, R.E. Trouwborst, T.S. Moore, E. Metzger, C. Kraiya, T.J. Waite, G. Druschel, B. Sundby, and others. 2008. "Use of Voltammetric Solid-State (Micro)Electrodes for Studying Biogeochemical Processes: Laboratory Measurements to Real Time Measurements with an in situ Electrochemical Analyzer (ISEA)," *Marine Chemistry*, 108, 221-235.
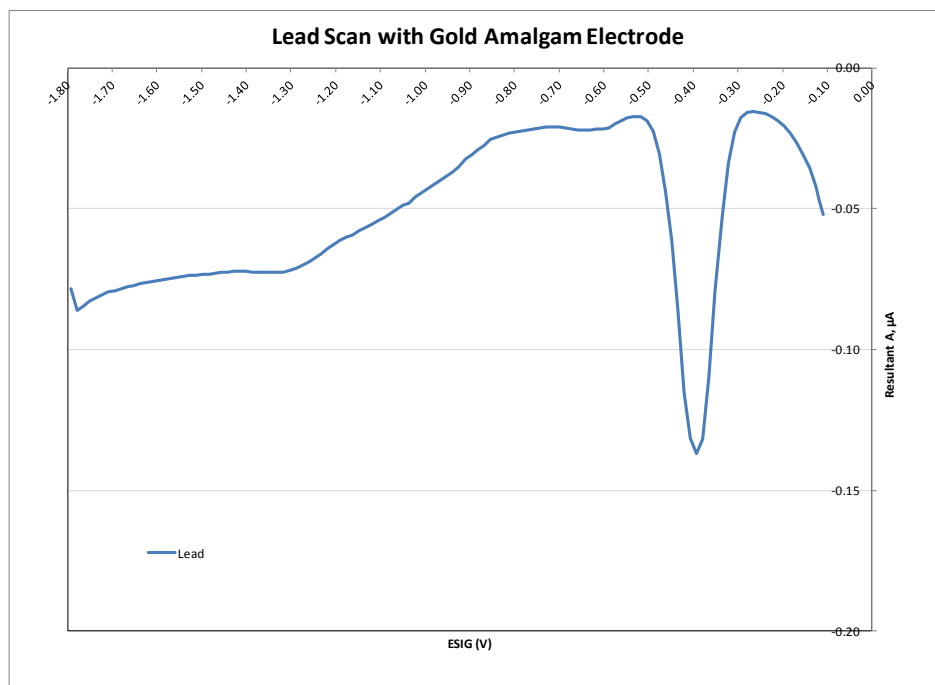
APPENDIX A

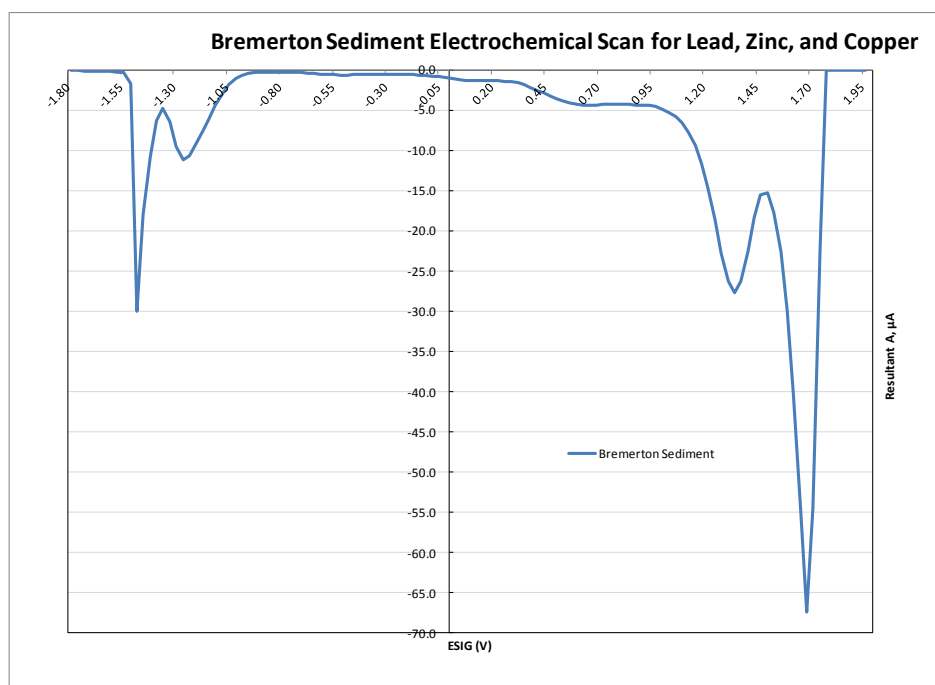**Representative Poor Electrochemical Scans**
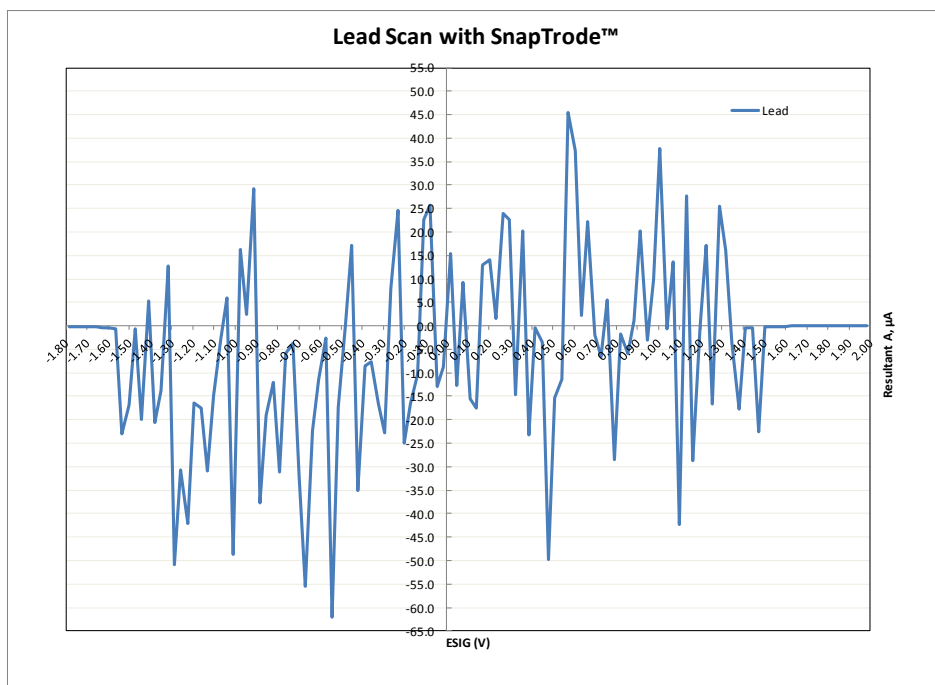
Figure A1. Poor Lead Electrochemical Scans with SnapTrode™ in Standard Solution
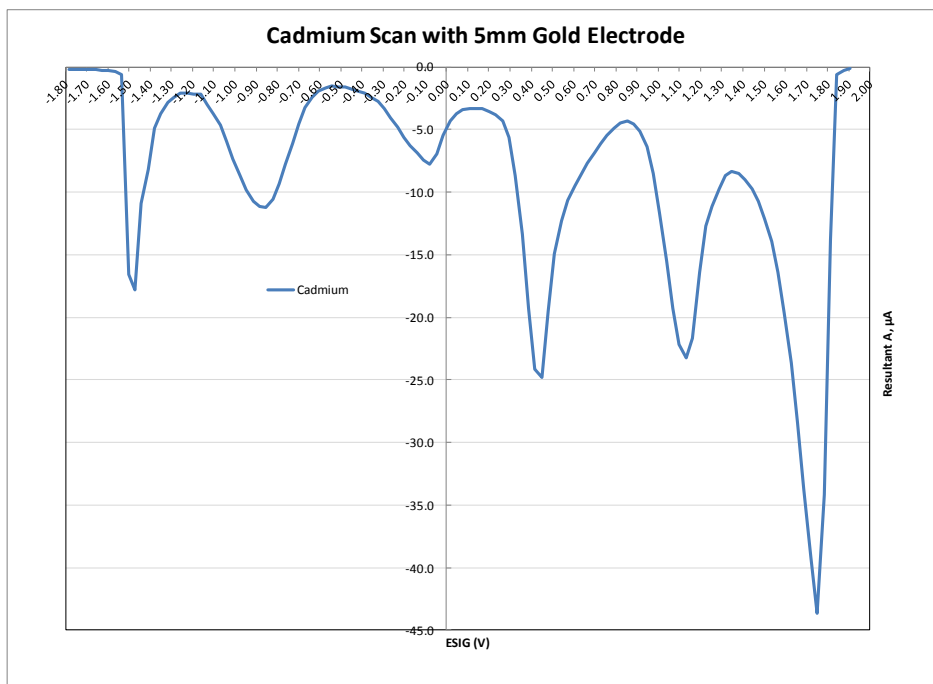
Figure A2. Poor Cadmium Electrochemical Scans with 5 mm Gold Electrode in Standard Solution
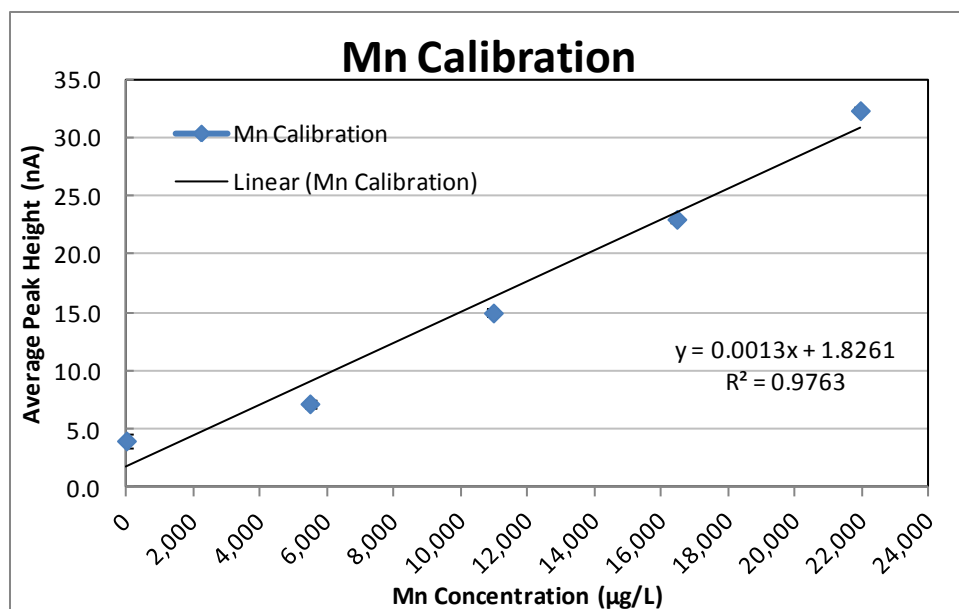
Figure A3. Poor Lead Electrochemical Scans with Gold-Mercury Amalgam Electrode in Standard Solution

Figure A4. Poor Electrochemical Scan with 5 mm Gold Electrode in Bremerton Sediment
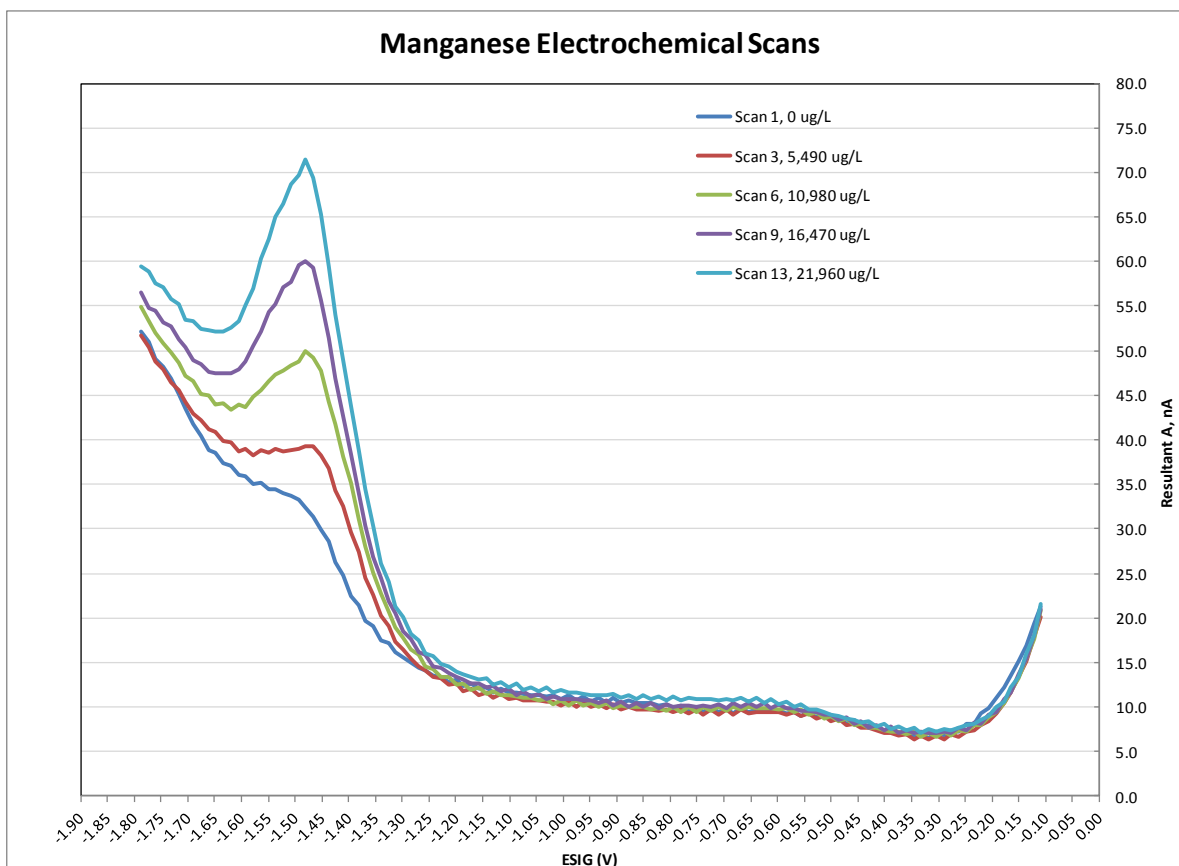
APPENDIX B

Standard Solution Test Data

Figure B1. Manganese Calibration Curve in Standard Solutions

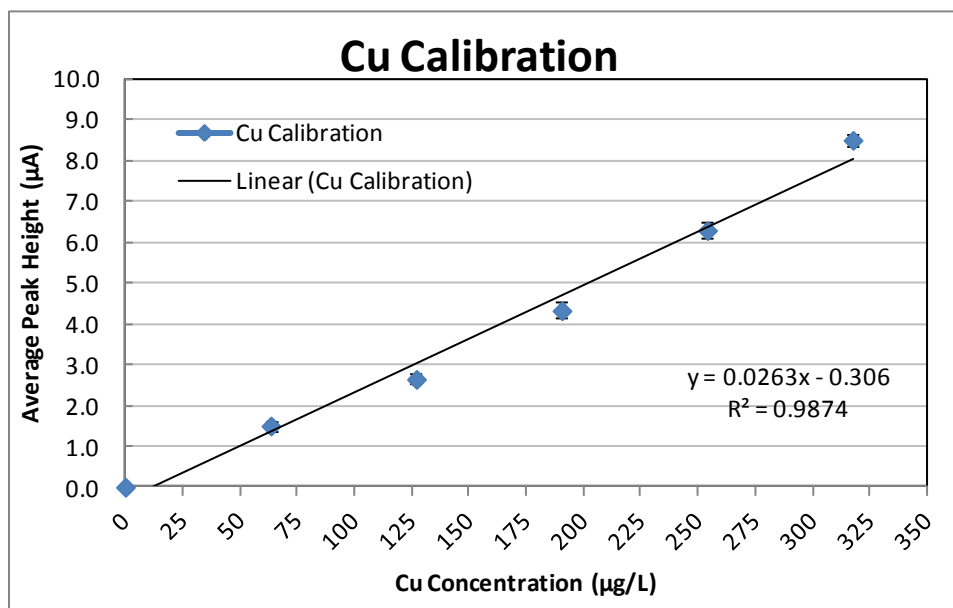**Table B1. Manganese Calibration Scan Data in KCL Standard Solution**

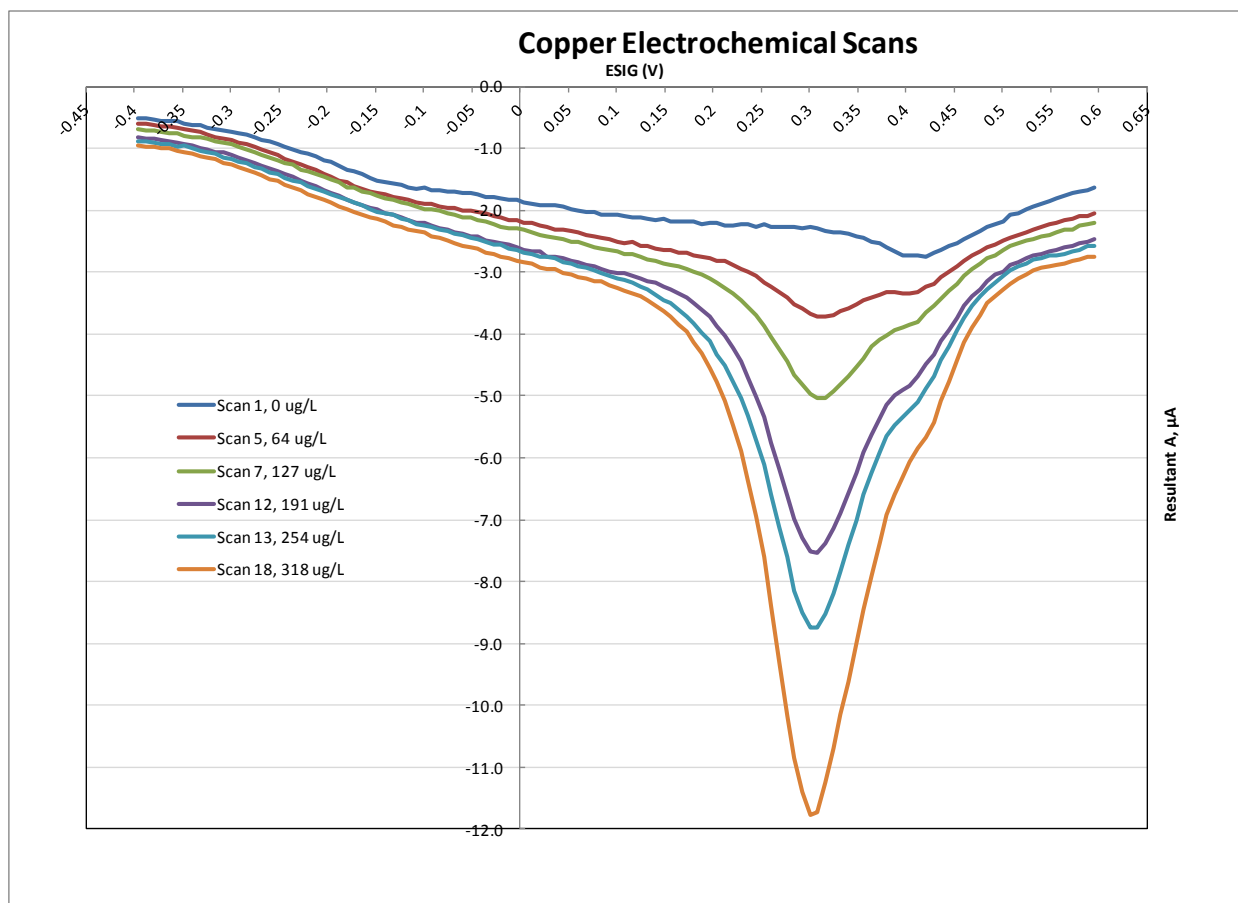| Concentration (μM)	Concentration (μg/L)	Peak Height (nA)	Peak Coordinates (x,y)	Scan ID	Average Peak Height (nA)	Standard Deviation (nA)	Coefficient of Variation (%)
0	0	4.64	(-1.484,32.060)	1	4.03	0.87	21.61
		3.41	(-1.442, 29.7)	2			
		-	-	-			
100	5,490	6.65	(-1.474, 39.150)	3	7.21	0.65	9.06
		7.05	(-1.472, 39.9)	4			
		7.92	(-1.479, 40.68)	5			
200	10,980	14.80	(-1.484, 49.7)	6	14.99	0.62	4.12
		14.49	(-1.486, 49.48)	7			
		15.69	(-1.481, 50.35)	8			
300	16,470	22.60	(-1.489,60.08)	9	23.03	0.47	2.05
		23.53	(-1.484, 60.91)	10			
		22.94	(-1.493, 61.11)	11			
400	21,960	31.87	(-1.491, 69.39)	12	32.35	0.42	1.29
		32.56	(-1.486, 71.25)	13			
		32.62	(-1.486, 70.22)	14			

Figure B2. Manganese Electrochemical Scans in Standard Solutions
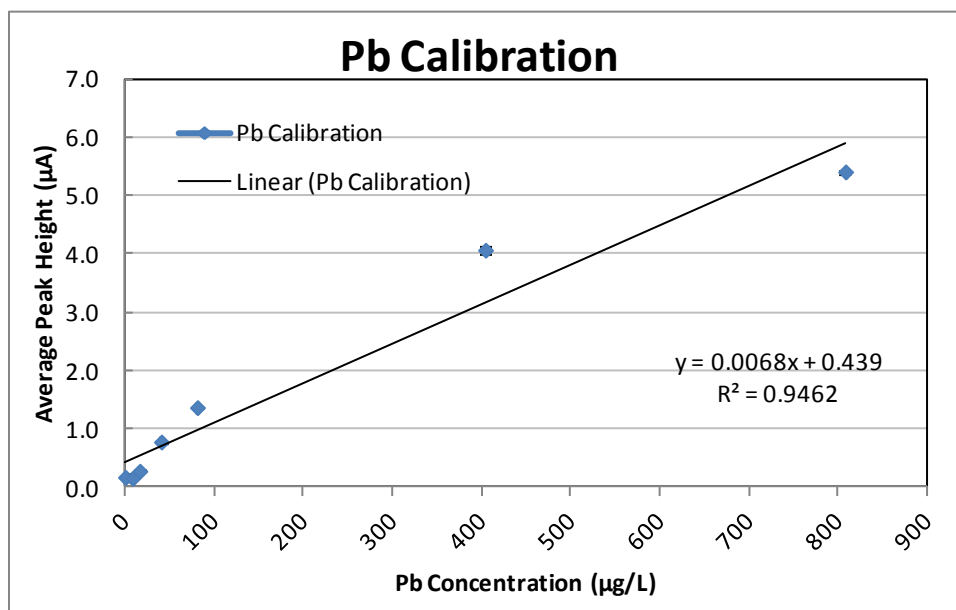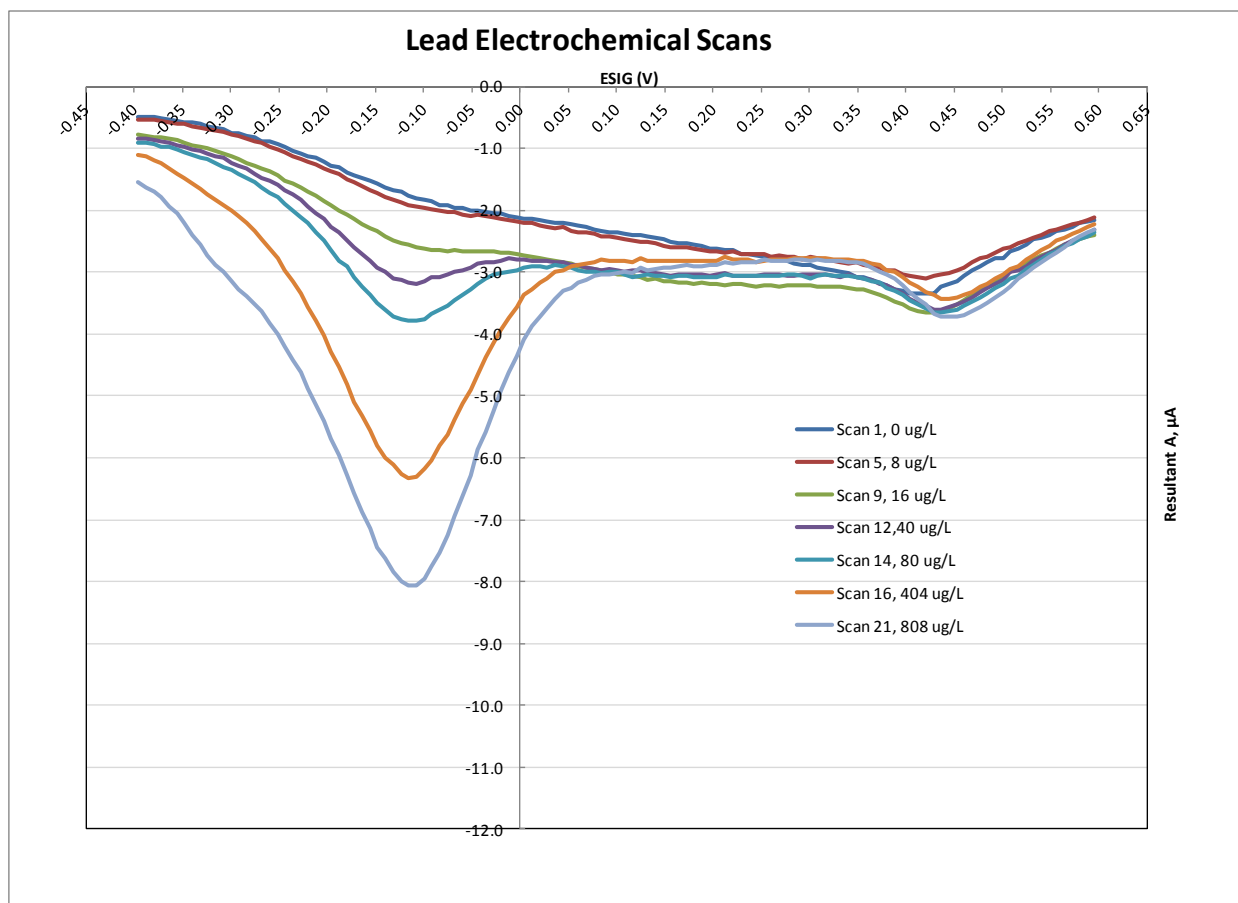

Figure B3. Copper Calibration Curve in Standard Solutions

Table B2. Copper Calibration Scan Data in KCL Standard Solution

Concentration (μM)	Concentration (μg/L)	Peak Height (nA)	Peak Coordinates (x,y)	Scan ID	Average Peak Height (nA)	Standard Deviation (nA)	Coefficient of Variation (%)
0	0	0	0.00	1	0.00	0.00	-
		0	0.00	2			
		0	0.00	3			
1	64	1.7	(0.307, -4.179)	4	1.50	0.20	13.3
		1.3	(0.31, -3.702)	5			
		1.5	(0.314, -4.041)	6			
2	127	2.43	(0.309, -5.011)	7	2.64	0.22	8.1
		2.64	(0.307, -5.182)	8			
		2.86	(0.31, -5.478)	9			
3	191	3.98	(0.306, -6.635)	10	4.32	0.34	7.9
		4.33	(0.307, -7.117)	11			
		4.66	(0.304, -7.491)	12			
4	254	6.02	(0.309, -8.771)	13	6.29	0.33	5.3
		6.19	(0.307, -9.153)	14			
		6.66	(0.306, -9.714)	15			
5	318	8.21	(0.309, -11.27)	16	8.50	0.26	3.1
		8.58	(0.311, -11.63)	17			
		8.71	(0.304, -11.73)	18			

Copper Electrochemical Scans

Figure B4. Copper Electrochemical Scans in Standard Solutions

Pb Calibration
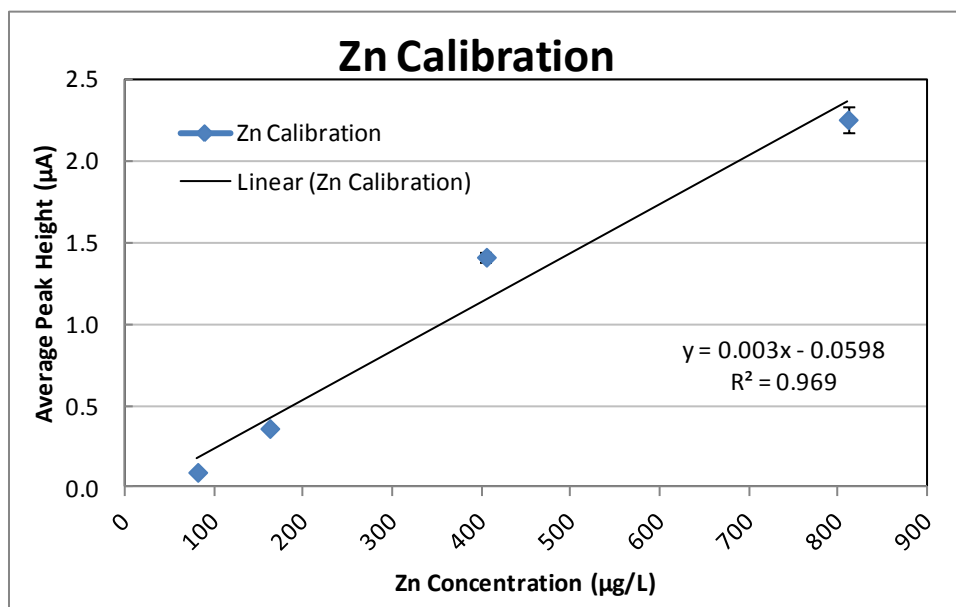
$y = 0.0068x + 0.439$

$R^2 = 0.9462$

Figure B5. Lead Calibration Curve in Standard Solutions

Table B3. Lead Calibration Scan Data in KCL Standard Solution

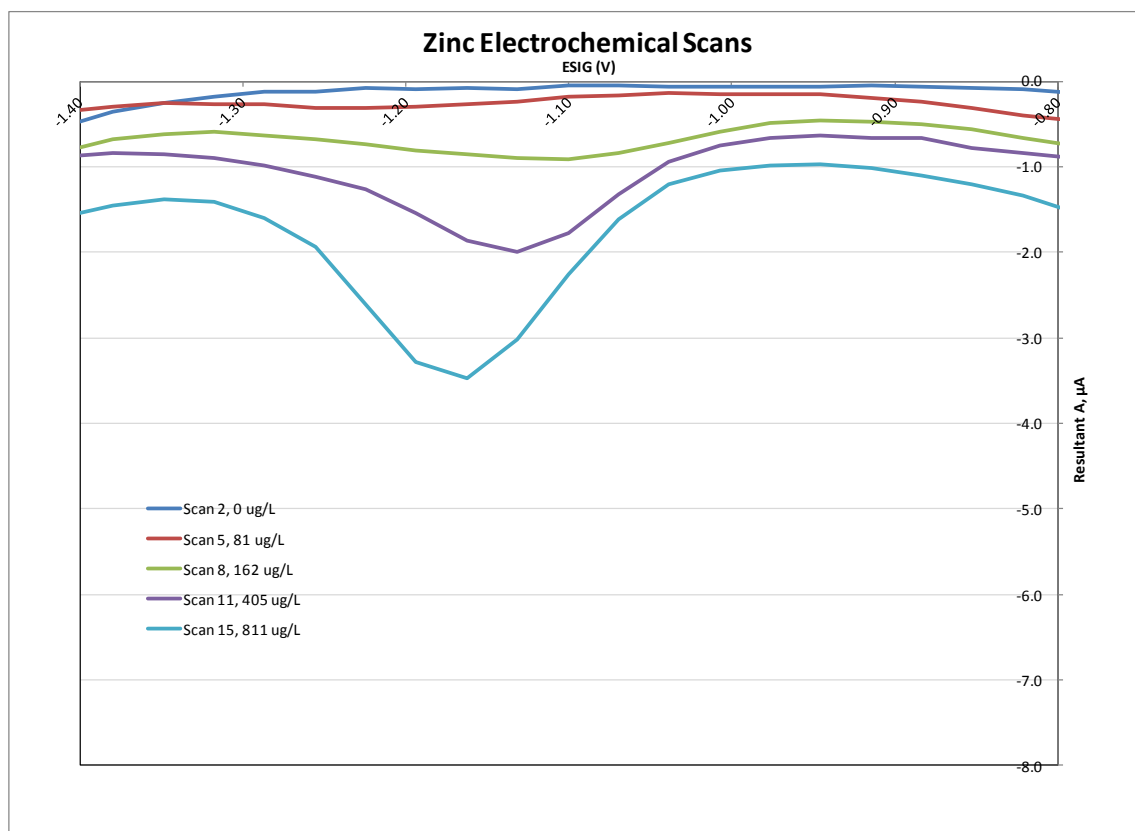| Concentration (μM)	Concentration (μg/L)	Peak Height (nA)	Peak Coordinates (x,y)	Scan ID	Average Peak Height (nA)	Standard Deviation (nA)	Coefficient of Variation (%)
0	0	0.25	(-0.07, -1.21)	1	0.17	0.13	76.61
		0.02	(-0.119, -1.704)	2			
		0.25	(-0.1, -1.813)	3			
39	8.1	0.16	(-0.129, -1.832)	4	0.16	0.02	9.75
		0.17	(-0.124, -2.125)	5			
		0.14	(-0.125, -2.177)	6			
78	16.2	0.26	(-0.125, -2.248)	7	0.28	0.03	9.45
		0.31	(-0.115, -2.42)	8			
		0.27	(-0.118, -2.535)	9			
195	40.4	0.80	(-0.121, -2.995)	10	0.78	0.03	3.39
		0.75	(-0.122, -3.068)	11			
		0.79	(-0.114, -3.152)	12			
390	80.8	1.37	(-0.112, -3.793)	13	1.37	0.01	0.73
		1.38	(-0.114, -3.777)	14			
		1.36	(-0.11, -3.71)	15			
1,950	404	4.00	(-0.112, -6.323)	16	4.07	0.13	3.19
		3.99	(-0.119, -6.41)	17			
		4.22	(-0.115, -6.542)	18			
3,900	808	5.39	(-0.115, -7.957)	19	5.41	0.06	1.08
		5.37	(-0.114, -7.992)	20			
		5.48	(-0.11, -8.071)	21			

Figure B6. Lead Electrochemical Scans in Standard Solutions

Figure B7. Zinc Calibration Curve in Standard Solutions

B-6

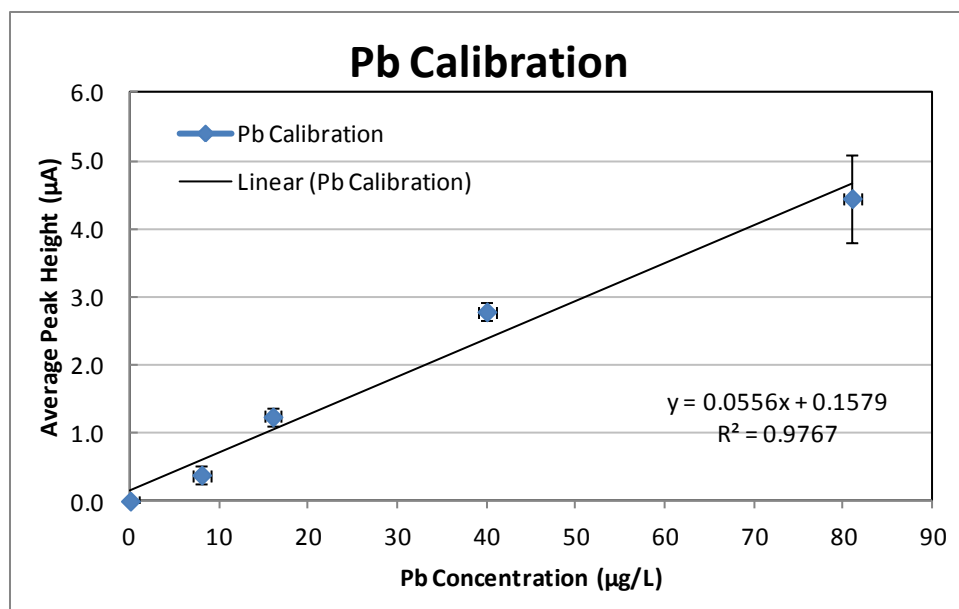**Table B4. Zinc Calibration Scan Data in KCL Standard Solution**

Concentration (µM)	Concentration (µg/L)	Peak Height (nA)	Peak Coordinates (x,y)	Scan ID	Average Peak Height (nA)	Standard Deviation (nA)	Coefficient of Variation (%)
0	0	0.00	-	1	0.00	0.00	0.00
		0.00	-	2			
		0.00	-	3			
1.24	81	0.08	(-1.172, -0.3083)	4	0.09	0.02	23.51
		0.12	(-1.199, -0.3228)	5			
		0.08	(-1.219, -0.3307)	6			
2.48	162	0.30	(-1.18, -0.7399)	7	0.36	0.06	15.98
		0.37	(-1.099, -0.9002)	8			
		0.41	(-1.071, -0.9002)	9			
6.2	405	1.52	(-1.11, -2.372)	10	1.41	0.13	9.28
		1.26	(-1.118, -1.988)	11			
		1.45	(-1.11, -2.276)	12			
12.4	811	2.21	(-1.153, -3.489)	13	2.25	0.04	1.57
		2.28	(-1.153, -3.453)	14			
		2.27	(-1.157, -3.475)	15			

Figure B8. Zinc Electrochemical Scans in Standard Solution

APPENDIX C
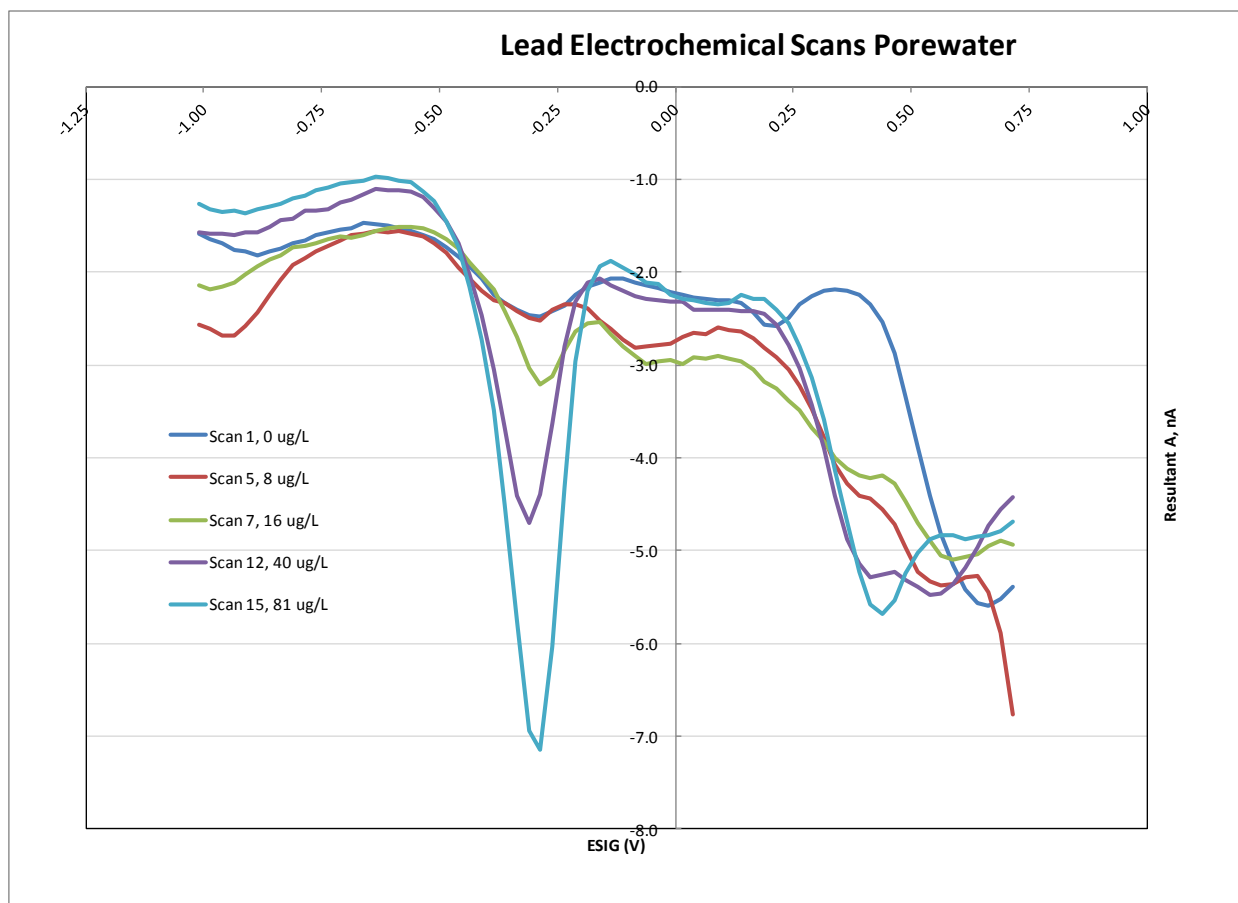
Bremerton Porewater Test Data

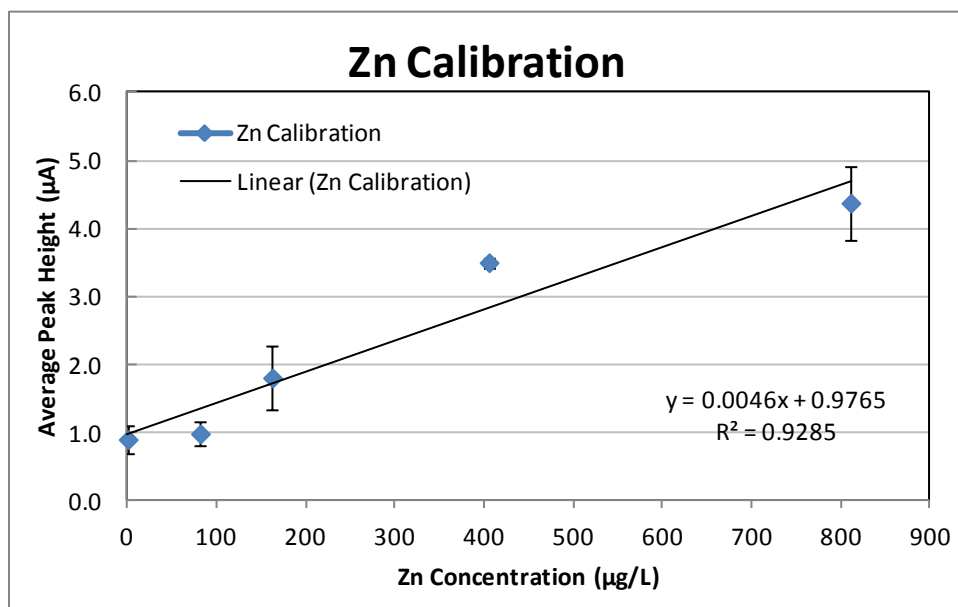**Figure C1. Lead Calibration Curve in Bremerton Porewater**

Table C1. Lead Calibration Scan Data in Bremerton Porewater

| Concentration (µM)	Concentration (µg/L)	Peak Height (nA)	Peak Coordinates (x,y)	Scan ID	Average Peak Height (nA)	Standard Deviation (nA)	Coefficient of Variation (%)
0	0	0.00	-	1	0.00	0.00	-
		0.00	-	2			
		0.00	-	3			
39	8	0.17	(-0.275, -2.338)	4	0.38	0.24	61.88
		0.34	(-0.2875, -2.512)	5			
		0.64	(-0.2688, -2.82)	6			
78	16	0.97	(-0.2781, -3.198)	7	1.24	0.24	19.63
		1.31	(-0.2781, -3.552)	8			
		1.44	(-0.2969, -3.382)	9			
195	40	2.51	(-0.2781, -4.387)	10	2.78	0.24	8.76
		2.88	(-.2938, -4.587)	11			
		2.97	(-0.3031, -4.692)	12			
390	81	3.34	(-0.2875, -4.874)	13	4.45	1.13	25.37
		4.41	(-0.2938, -6.013)	14			
		5.59	(-0.2844, -7.169)	15			

Figure C2. Lead Electrochemical Scans in Bremerton Porewater

Figure C3. Zinc Calibration Curve in Bremerton Porewater

C-2

**Table C2. Zinc Calibration Scan Data in Bremerton Porewater**

| Concentration (µM)	Concentration (µg/L)	Peak Height (nA)	Peak Coordinates (x,y)	Scan ID	Average Peak Height (nA)	Standard Deviation (nA)	Coefficient of Variation (%)
0	0	0.48	(0.3894,-3.713)	1	0.90	0.36	40.47
		1.13	(0.3855, -3.94)	2			
		1.09	(0.4049, -3.782)	3			
1.24	81	0.69	(0.5211, -4.634)	4	0.98	0.31	31.24
		0.96	(0.494, -4.645)	5			
		1.30	(0.4708, -4.8)	6			
2.48	162	1.11	(0.5521, -4.705)	7	1.81	0.82	45.63
		1.59	(0.4863, -5.498)	8			
		2.72	(0.4863, -5.774)	9			
6.2	405	3.43	(0.48247, -6.484)	10	3.50	0.13	3.80
		3.41	(0.4591, -6.386)	11			
		3.65	(0.4746, -6.667)	12			
12.4	811	4.22	(0.4436, -7.135)	13	4.38	0.95	21.63
		3.51	(0.4591, -6.449)	14			
		5.39	(0.4514, -8.294)	15			
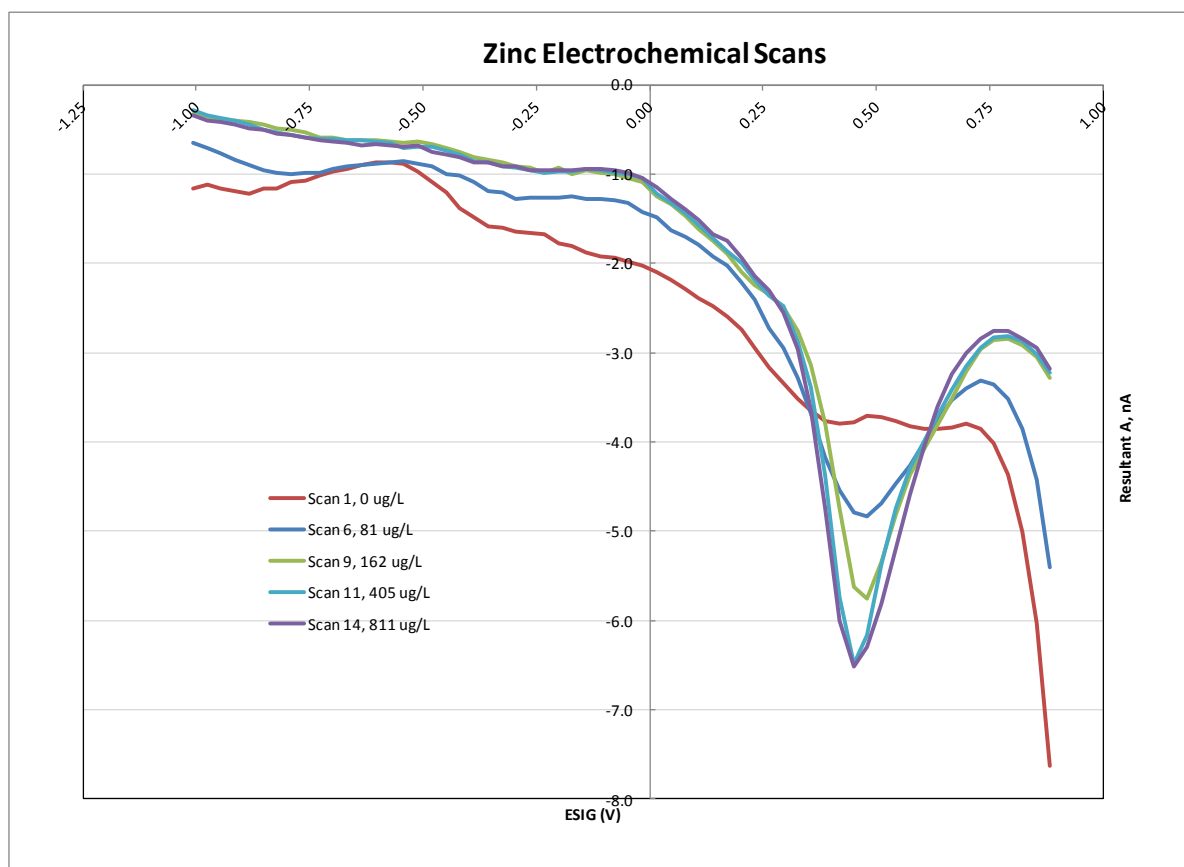
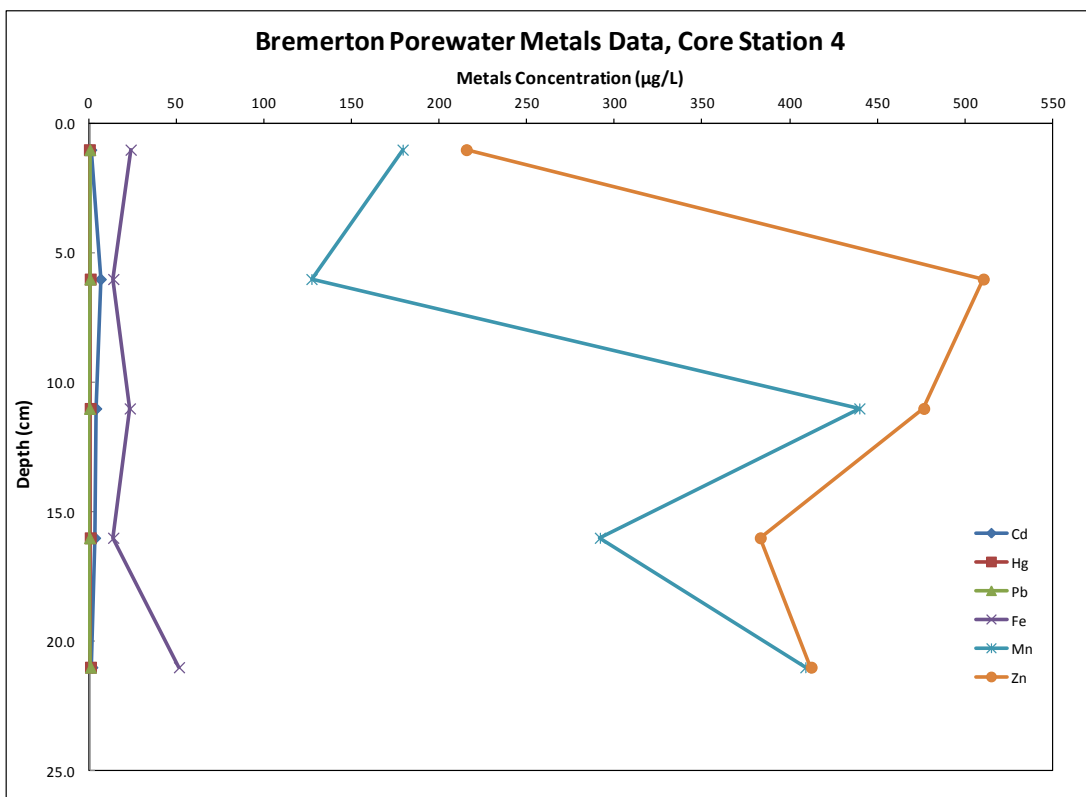**Figure C4. Zinc Electrochemical Scans in Bremerton Porewater**

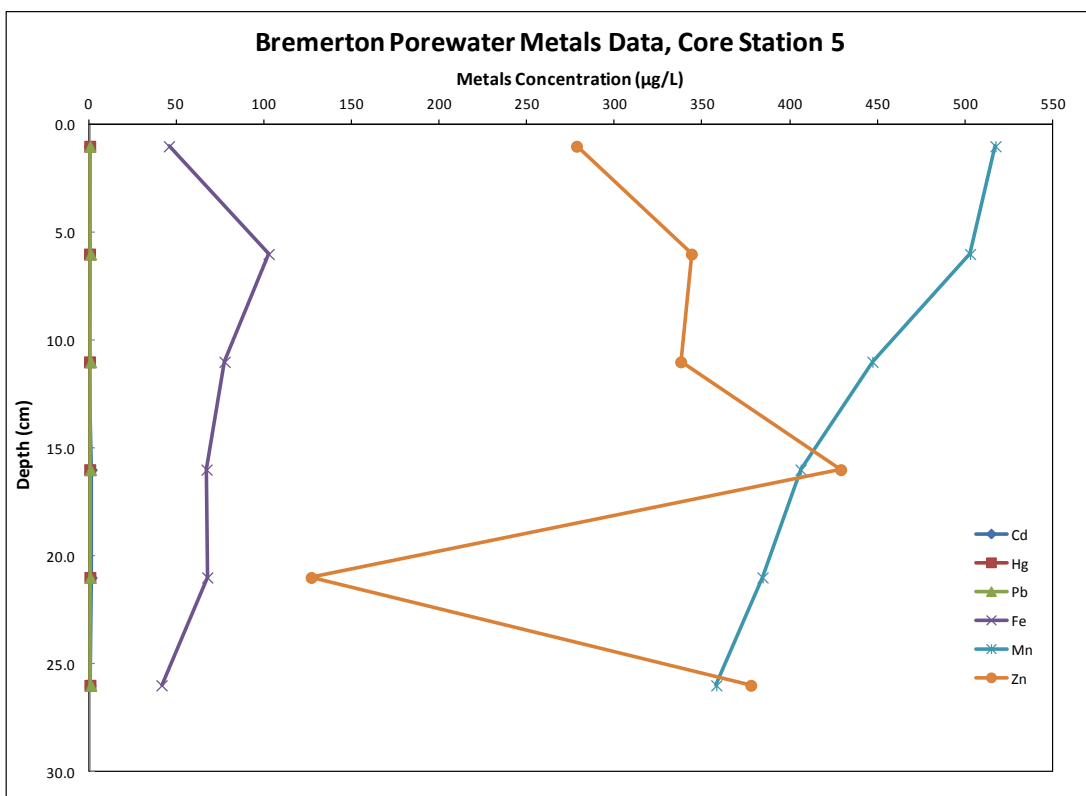**APPENDIX D**
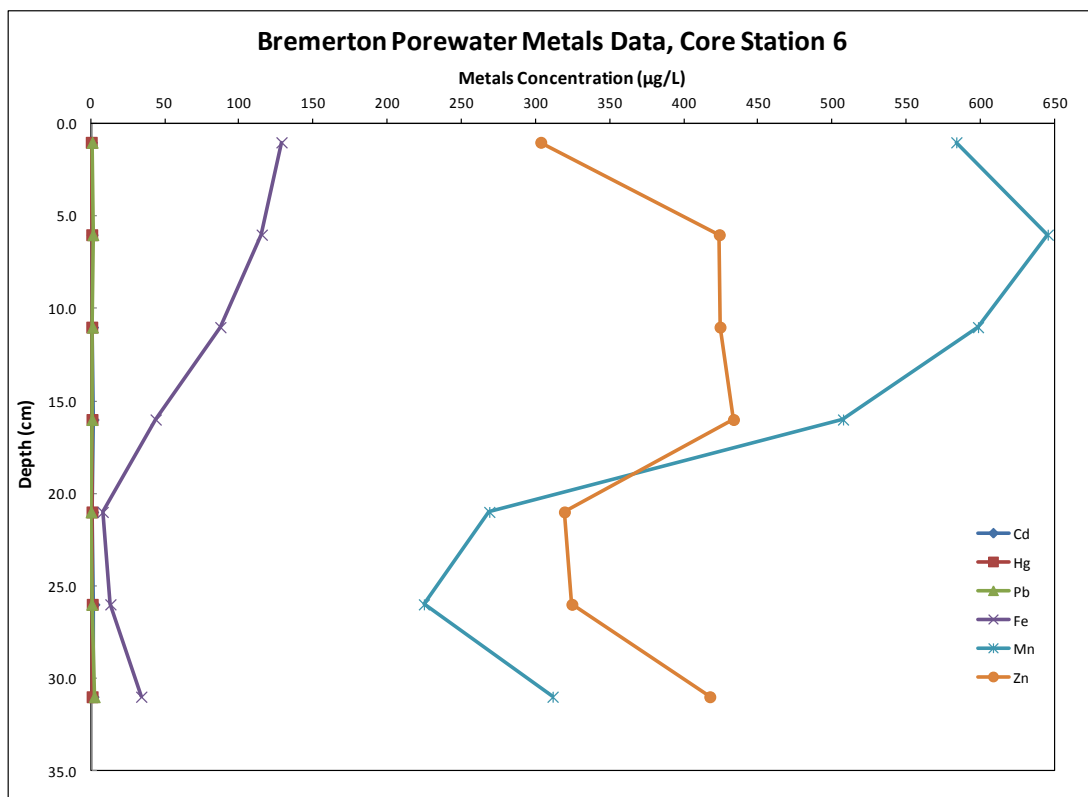
Porewater Characterization Data
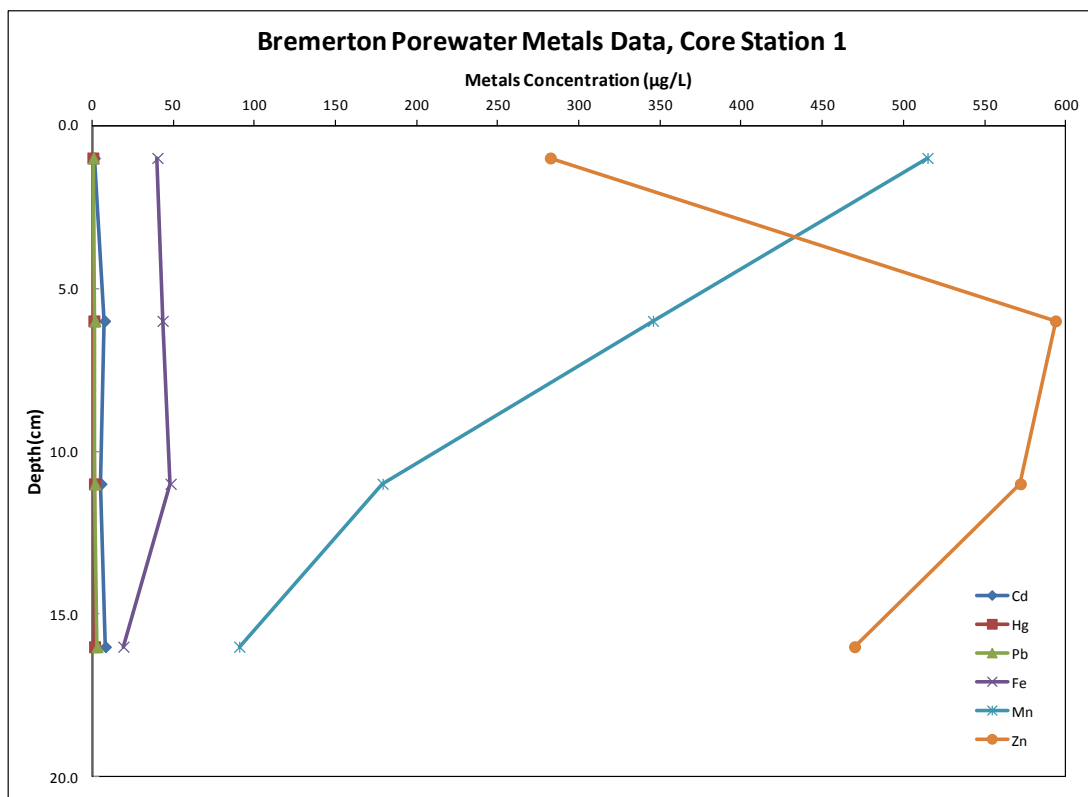
Figure D1. Metals Concentrations at Depth for Bremerton Porewater at Core Station 1
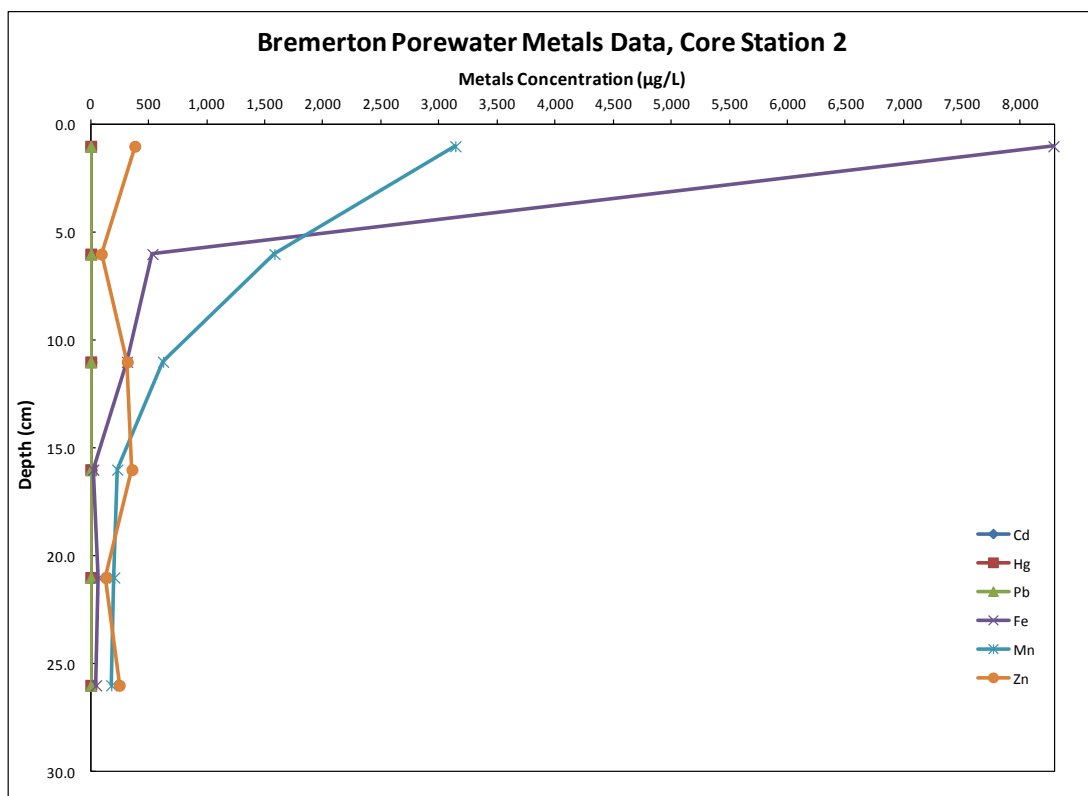
Figure D2. Metals Concentrations at Depth for Bremerton Porewater at Core Station 2

D-1

Figure D3. Metals Concentrations at Depth for Bremerton Porewater at Core Station 4

Figure D4. Metals Concentrations at Depth for Bremerton Porewater at Core Station 5
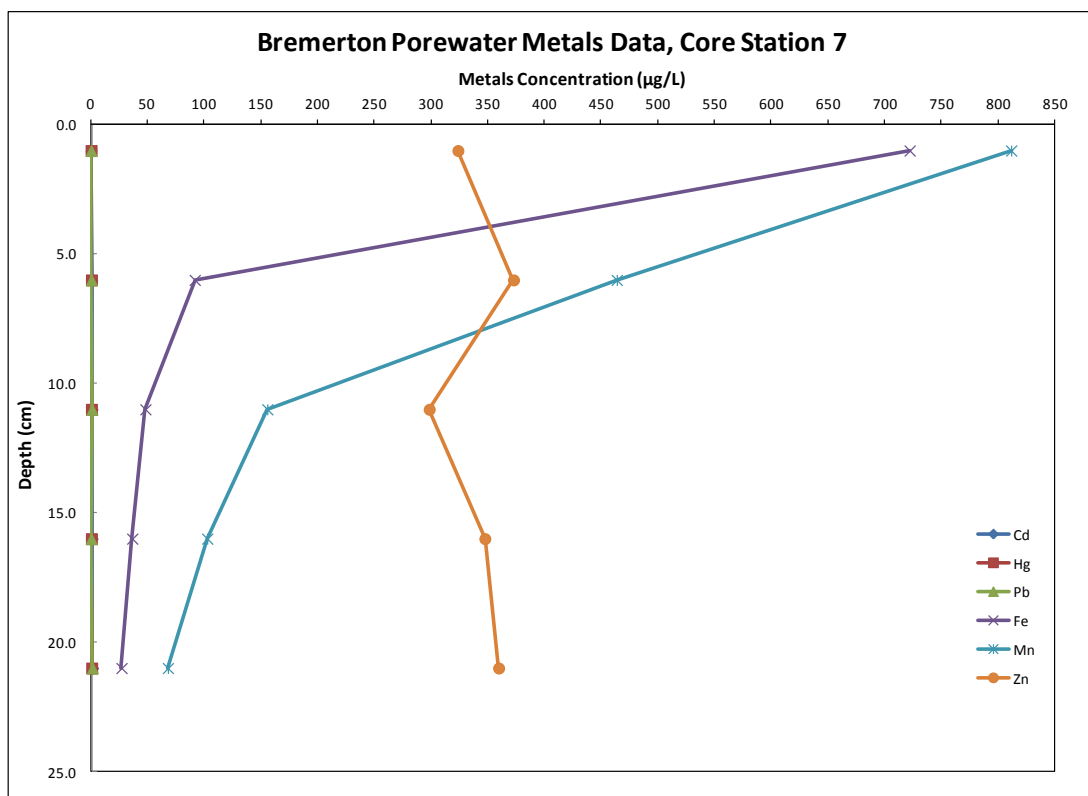
Figure D5. Metals Concentrations at Depth for Bremerton Porewater at Core Station 6
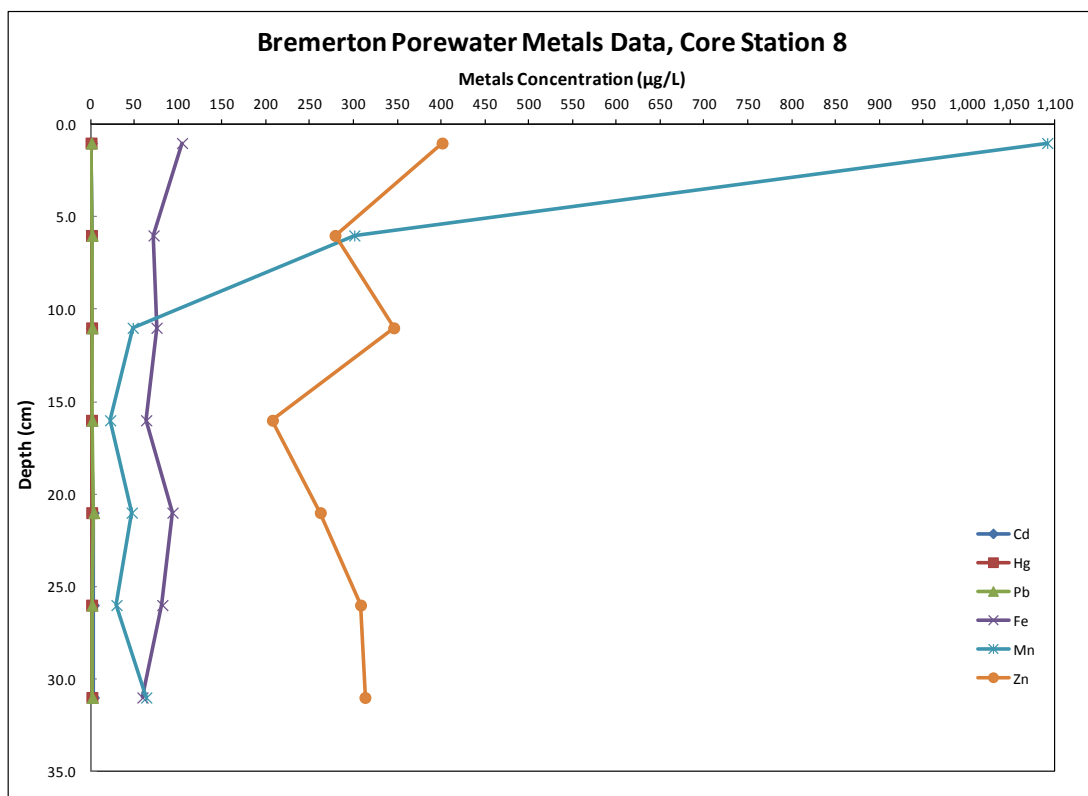

Figure D6. Metals Concentrations at Depth for Bremerton Porewater at Core Station 7

Figure D7. Metals Concentrations at Depth for Bremerton Porewater at Core Station 8

APPENDIX E
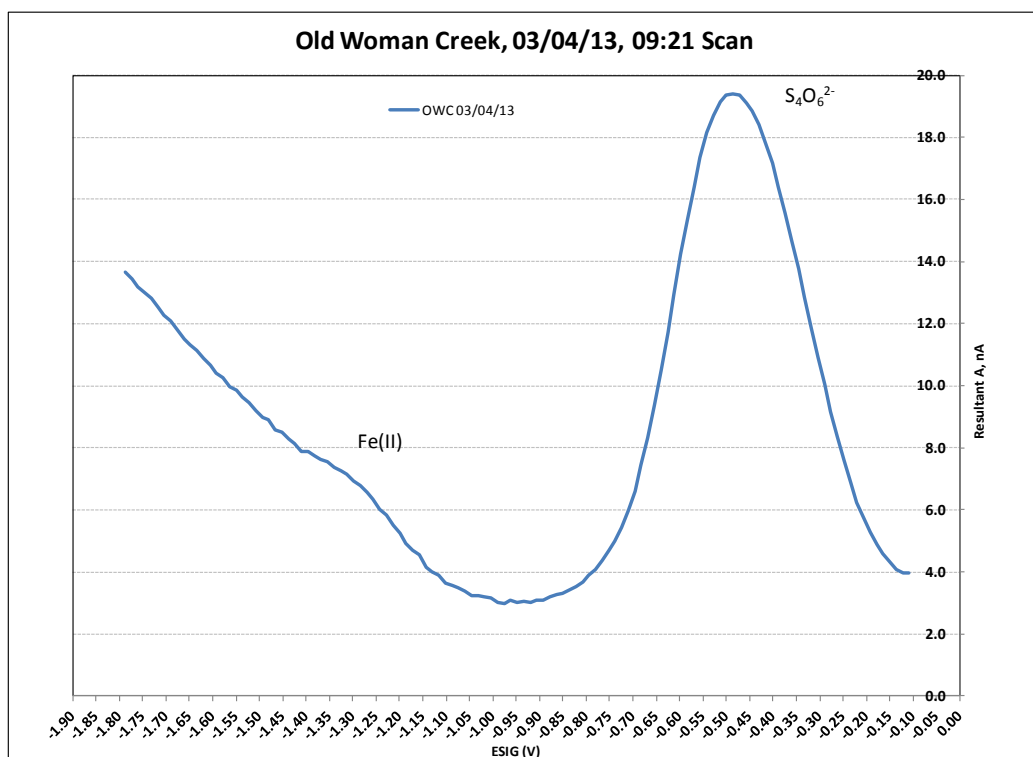
Old Woman Creek Deployment Data

Figure E1. Old Woman Creek Electrochemical Scan for March 3, 2013 at 9:21 A.M.

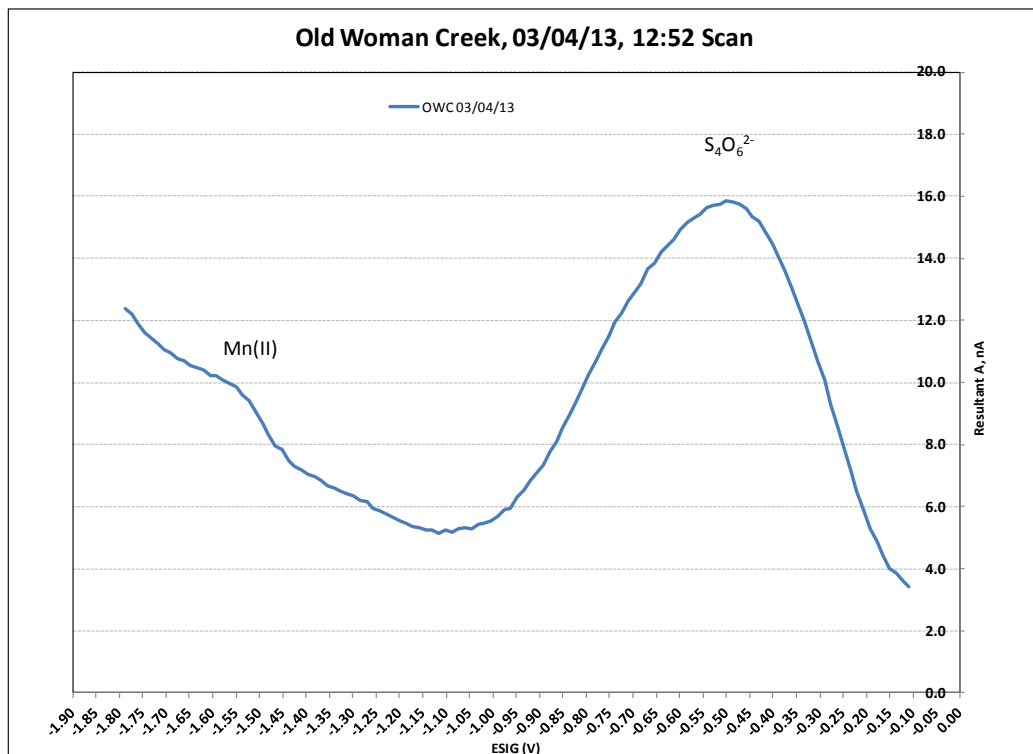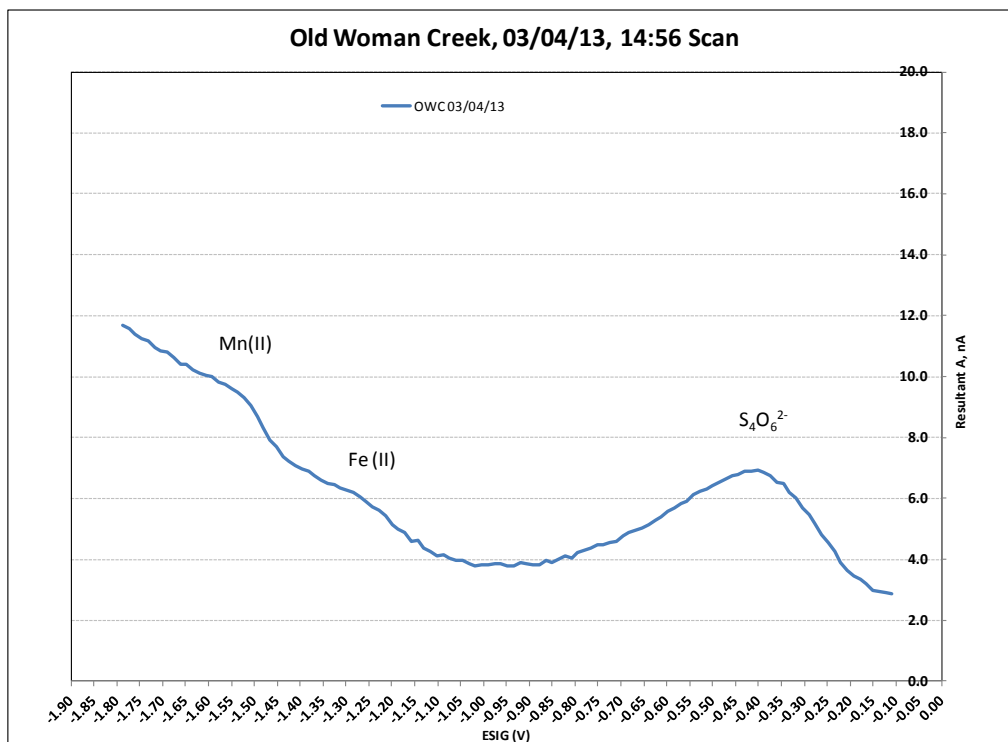**Figure E2. Old Woman Creek Electrochemical Scan for March 3, 2013 at 12:52 P.M.**

E-1

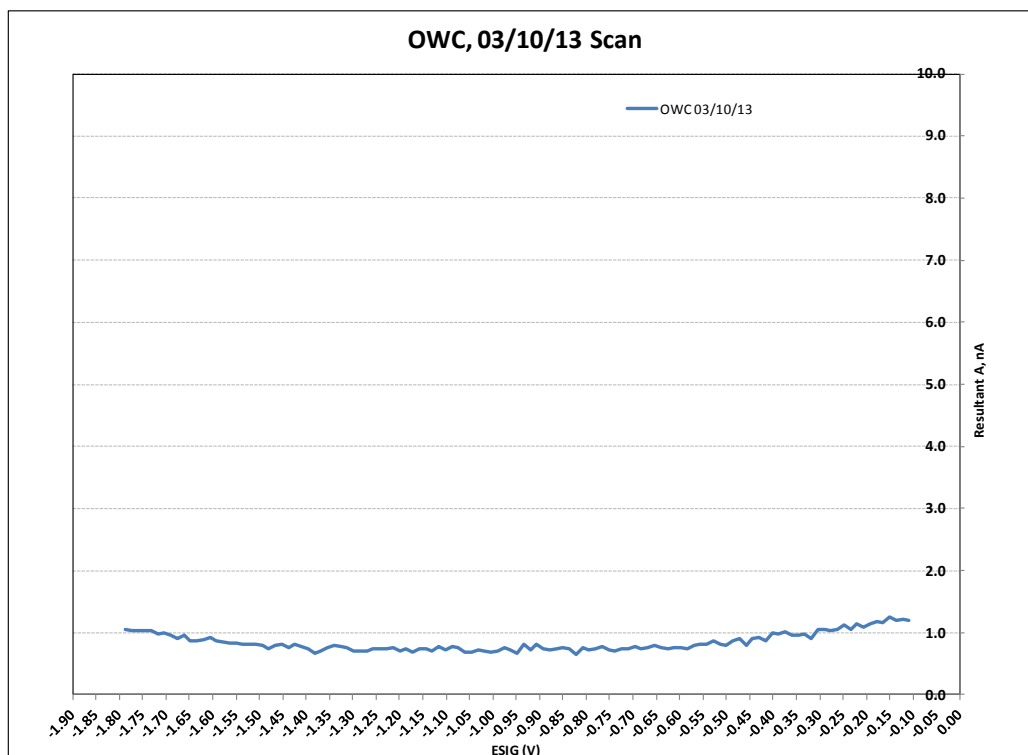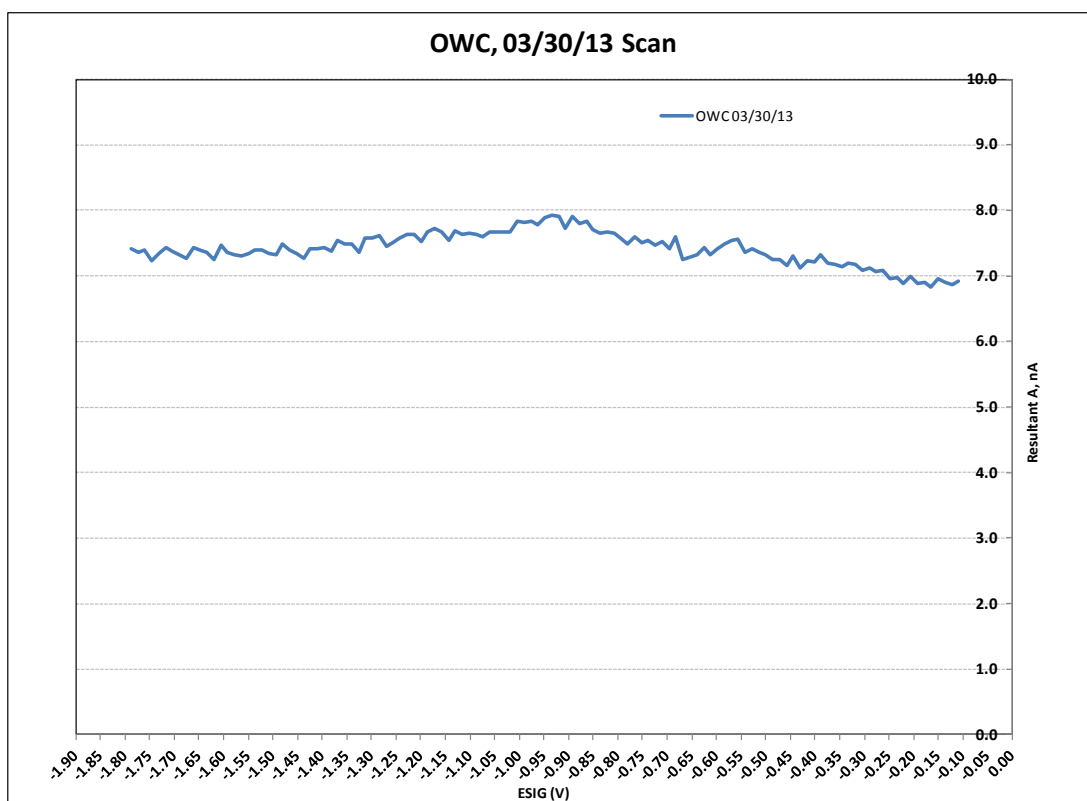**Figure E3. Old Woman Creek Electrochemical Scan for March 3, 2013 at 14:56 P.M.**

Figure E4. Old Woman Creek Representative Poor Electrochemical Scan for March 10, 2013

Figure E5. Old Woman Creek Representative Poor Electrochemical Scan for March 30, 2013

APPENDIX F

Bremerton Porewater Data

Table F1. Bremerton Porewater Data (Core 1 and 2)

Metals	Core 1 Depth				Core 2 Depth					
	1 cm	6 cm	11 cm	16 cm	1 cm	6 cm	11 cm	16 cm	21 cm	26 cm
	Sample ID				Sample ID					
	H1	H2	H3	H4	G1	G2	G3	G4	G5	G6
	µg/L				µg/L					
Cd	1.3	7.7	5.4	8.1	0.6	1.9	2.7	4.9	3.4	6.2
Hg	0.4	1.0	1.4	1.4	0.4	0.9	0.8	1.0	1.1	1.2
Pb	0.7	1.7	1.7	3.0	0.5	2.8	0.6	1.0	1.4	1.3
Fe	40.2	43.4	48.3	19.2	8,290	532	313	21.8	68.7	46.3
Mn	515	346	179	90.6	3,140	1,583	624	229	203	177
Zn	282	594	572	470	380	91.6	315	356	131	246

Table F2. Bremerton Porewater Data (Core 4 and 5)

Metals	Core 4 Depth					Core 5 Depth					
	1 cm	6 cm	11 cm	16 cm	21 cm	1 cm	6 cm	11 cm	16 cm	21 cm	26 cm
	Sample ID					Sample ID					
	B1	B2	B3	B4	B5	C1	C2	C3	C4	C5	C6
	µg/L					µg/L					
Cd	1.3	6.7	4.1	3.5	1.9	0.3	0.6	0.5	1.5	1.5	0.9
Hg	0.4	0.9	0.9	0.9	1.0	0.6	0.5	0.5	0.6	0.7	0.7
Pb	0.7	0.7	0.5	0.5	1.1	0.8	1.1	1.2	1.0	0.9	1.2
Fe	24.0	14.0	23.5	14.0	51.6	45.8	102.7	77.5	67.3	67.7	41.6
Mn	179	127	440	292	409	517	503	447	406	385	358
Zn	215	510	476	383	412	278	344	338	429	127	378

Table F3. Bremerton Porewater Data (Core 6 and 7)

Metals	Core 6 Depth							Core 7 Depth				
	1 cm	6 cm	11 cm	16 cm	21 cm	26 cm	31 cm	1 cm	6 cm	11 cm	16 cm	21 cm
	Sample ID							Sample ID				
	D1	D2	D3	D4	D5	D6	D7	E1	E2	E3	E4	E5
	µg/L							µg/L				
Cd	0.6	1.0	1.3	1.6	1.4	2.2	1.6	0.3	1.0	1.3	1.4	1.8
Hg	0.4	0.7	0.8	0.9	0.9	1.1	1.0	0.4	0.7	0.7	0.7	0.9
Pb	1.0	1.5	1.2	0.9	0.3	0.7	2.4	0.4	0.6	1.2	0.5	1.5
Fe	129	115	87.5	43.9	8.1	13.3	34.1	722	91.8	48.3	36.6	27.2
Mn	584	645	598	507	269	225	312	812	464	156	103	68.2
Zn	304	424	424	433	319	325	418	324	373	299	348	360

Table F4. Bremerton Porewater Data, Core 8

Metals	Core 8 Depth						
	1 cm	6 cm	11 cm	16 cm	21 cm	26 cm	31 cm
	Sample ID						
	F1	F2	F3	F4	F5	F6	F7
	µg/L						
Cd	0.8	1.2	0.8	0.9	3.0	3.0	3.2
Hg	0.4	0.9	1.1	1.0	1.2	1.1	1.4
Pb	0.9	1.7	1.8	1.7	3.6	1.6	1.9
Fe	104	71.8	75.2	63.3	93.4	81.8	59.2
Mn	1,092	301	48.1	22.2	46.9	29.5	63.4
Zn	401	279	346	207	262	308	313